STUDIES IN THE MASS SPECTRA OF PERFLUOROAROMATIC DERIVATIVES OF PHOSPHORUS AND SOME SELECTED TRANSITION METALS

By

Timothy R.B. Jones B.Sc.

A thesis submitted to the Department of Chemistry
in partial fulfillment of the requirements for
the degree of Master of Science.

Brock University
St. Catharines, Ontario

April, 1975

ABSTRACT

The mass spectra and fragmentation of a variety of fluoroaromatic compounds of Group V and some selected transition elements are discussed in some detail, aided by data from metastable defocussed experiments. Results of studies on the coupling reaction using unstable organo-titanium chloride intermediate species are reported. The preparation of some 5-substituted octafluorodibenzophospholes is also discussed. Rearrangements under electron bombardment resulting in the loss of heteroatom-fluoride fragments are discussed in the light of presently accepted mechanisms for these processes as are rearrangements observed in compounds involving thionophosphoryl bonds (P=S).

ACKNOWLEDGEMENTS

The author would like to express his great appreciation to Professor J.M. Miller, the supervisor of this work for his constant encouragement and helpful discussions, to his wife Janice for her unfaltering confidence and support, the rest of his family and members of the department and staff, especially Messrs. G.L. Wilson, P. Bickart, M.S. Gibson and J. Vandenhoff.

Finally, he would like to thank Professors M. Fild, D.W. Meek and M.D. Rausch for the provision of most of the samples used in this study.

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INTRODUCTION

Mass Spectra of Perfluoroaromatic Compounds

Over the past decade there has been a great upsurge in the use of mass spectrometry with regards to analysis of all types of inorganic and organometallic compounds. Previously, many of these species were not considered compatible with mass spectrometry due to poor sampling and handling techniques as well as problems involved with decomposition in the source regions. As a result of advances in instrumentation and sampling techniques a great variety of these species can now be dealt with efficiently by mass spectrometric methods.

Aside from direct analytical procedures, two other important aspects have arisen with respect to the mass spectra of these compounds. The role of the heteroatom(s) in cleavage processes and the reflection of the direction of bond-breaking and/or subsequent rearrangements can add valuable information to molecular structure and bonding data obtained from other techniques. The development of trends with respect to compound classes and the behaviour of the molecular ion in these cases are continually being investigated to extend our knowledge of these factors and assist in future identification of unknown quantities with the aid of interfaced computer systems. Continual enhancement of these varied processes has already proved vital in

solving problems related to trace-level analysis of pollutants, insecticide residues and drug overdoses.[1,2]

The purpose of the work presented here is two-fold. In contrast to our rather extensive knowledge of amines[3,4] relatively little mass spectral data has been compiled on either aliphatic or aromatic phosphines including their halides, oxides and sulfides.

The role of phosphorus in the fragmentation process in these systems is not clearly understood but one obvious feature is a pronounced cleavage of the carbon-phosphorus bond due to the greater ability of the phosphorus atom to accommodate a positive charge. There is also well-documented evidence for extensive hydrogen rearrangement in both alkyl[6] and aryl systems. This latter observation is related to the second motive behind this work, investigation of other rearrangements occurring in these systems. Included in this theme are several processes involving bond formation between substituents as well as transfer of atoms to phosphorus itself. The limited earlier research in this realm demonstrated the tendency for such rearrangements to occur with various organophosphorus sulfides[61] and a variety of perhaloaromatic phosphines[13,14] and phosphine halides.[16]

In previous studies involving fluorine transfer rearrangements to the heteroatom during the breakdown process, the mechanism for such intramolecular transitions

has been a questionable topic. From the observed data it appears that vacant orbitals are required on the central atom since none of these rearrangements is observed for carbon[8], nitrogen[9], or oxygen[10] derivatives. Boron[11,12] with its vacant p-orbital as well as other main group[8-10, 13-16], and transition metal[13,17,18-23] elements which have empty d-orbitals available, give evidence for such fluorine transfers in the mass spectra of their fluoroaromatic compounds.

These observations are consistent with suggestions by Cavell and Dobbie[16] that halogen transfer rearrangements in trifluoromethyl phosphines arise from the interaction of non-bonding fluorine p-orbitals with vacant d-orbitals on phosphorous. However, Hawthorne et al.[17] have suggested that when there are unsaturated sigma-bonded organic ligands, the rearranged ions can be rationalized by assuming that the ligand becomes π-bonded to the metal during fragmentation. This suggestion is based on the migration of fluorine atoms to the metal atom from all the ortho, meta and para positions of monofluorophenyl manganese pentacarbonyls despite the fact that ortho migrations are most favoured. These latter workers also note that no ions with fluorine bonded to phosphorous are found in the spectrum of tris (p-fluorophenyl) phosphine and attribute this to the lack of formation of a suitable π-bonded intermediate.

The most significant data in dispute of the Hawthorne concept arises out of recent work by Miller et al.[9] Here, losses of MF_n (n = 1,2,3,4,) species were observed for a number of fused heterocyclic derivatives of Group IV. It is extremely difficult to imagine $\sigma \rightarrow \pi$ type transfers occuring in compounds of the type described in the latter paper as this route would require even more drastic rearrangements. However, as Fig. 1 demonstrates, cyclic intermediates and expansion of co-ordination of the metal atom leads to more reasonable pathways in explaining such transfers.

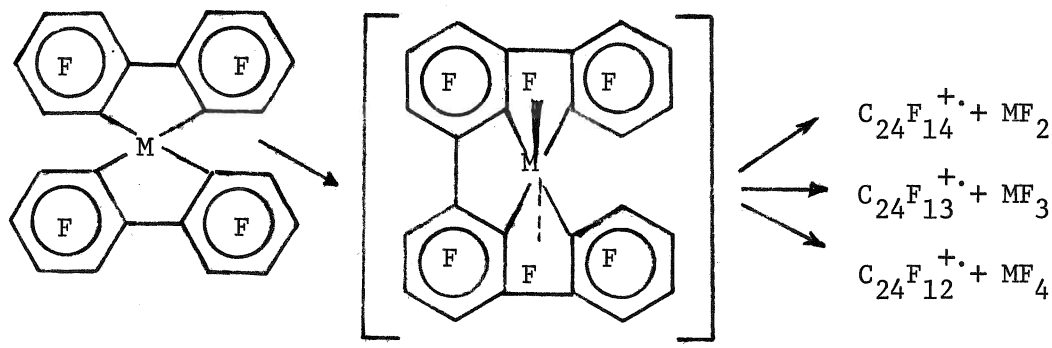

Fig. 1

When one considers the bulk of the evidence however, it is only possible to state preferences for either one or the other as little work has been done to prepare and analyze the proposed intermediates. To further our studies in this area, we have selected a number of perfluoro-aromatic

phosphines and transition-metal derivatives which should help to more clearly define the processes occuring in the mass spectra of these systems.

Metastable Defocusing Techniques

Normal metastable ions have long been regarded as useful aids in the interpretation of mass spectra. These ions arise in double-focusing instruments of Nier-Johnson geometry in the second field-free region between the electric and magnetic sectors (see Fig. 2) where the parent ion m_1 decomposes to give a daughter ion m_2 and a neutral fragment with the resulting metastable observed at an apparent mass $m^* = m_2^{\,2}/m_1$ #.

To increase the utility of these ions several defocusing techniques have been developed to enhance metastable ion sensitivity by removing normal ions. Of these the Barber-Elliot technique[24], Ion Kinetic Energy (IKE) Spectroscopy[25], and Mass Analyzed Ion Kinetic Spectroscopy (MIKES)[26] are the most important which have developed.

In the first of these, metastable ions formed in the first field-free region (α in Fig. 2) are focused on the collector by tuning the magnet to a particular ion, then increasing the accelerating voltage while holding the ESA

For proof see Appendix B

voltage constant. The resulting collector output is then recorded as a function of the accelerating voltage and as a result, the precursors to the ion tuned in by the magnet can be observed. If m_1 and m_2 represent the masses of the parent and daughter ion respectively, then $m_2/m_1 = V_0/V_1$ where V_0 and V_1 are the initial accelerating voltage and that required to tune the parent ion to the ESA energy. A later refinement of this technique, known as IKE Spectroscopy, also involves detection of α - region metastables but now these are recorded at the ion monitor between the ESA and the magnet by scanning the analyzer voltage while the accelerating voltage is held constant. The MIKES technique, which has also been described as the Direct Analysis of Daughter Ions (DADI) by Maurer[27], normally requires the interchange of source and collector positions in a double-focusing mass spectrometer of Nier-Johnson* geometry but Miller has shown[28] that this and other similar techniques are easily accessible on an AEI-MS30 mass spectrometer (standard model) without the extensive

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* In contrast to Mattauch-Herzog geometry as depicted in the schematics below.

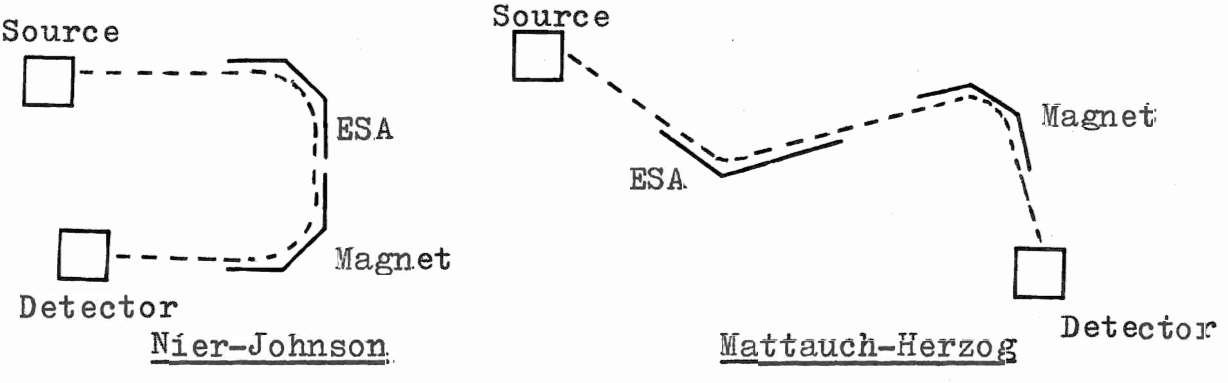
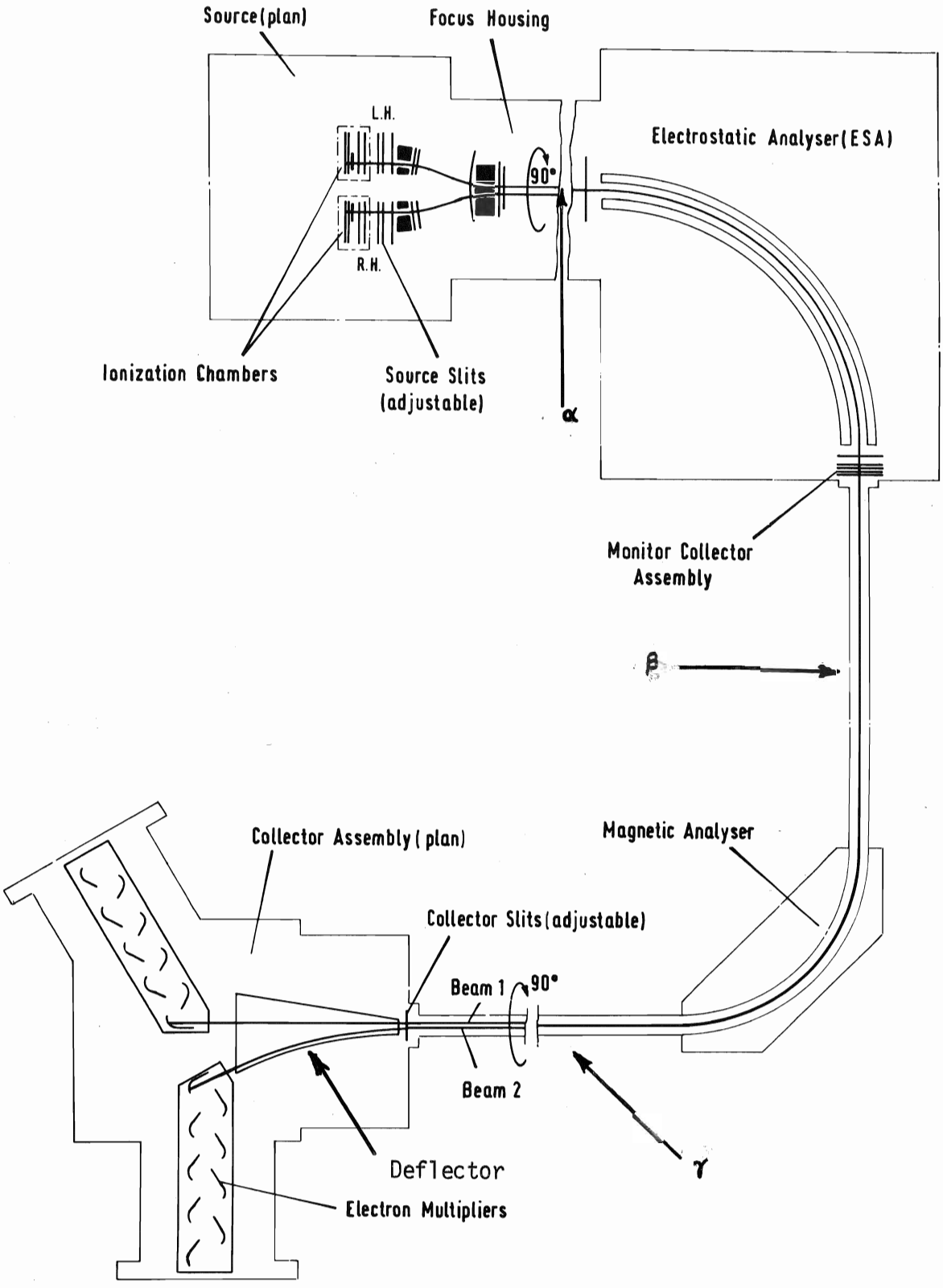


Figure 2
AEI MS30 Ion
Optics Schematic



Principle of Operation

alterations necessary with other commercial spectrometers[26,29]. The critical feature is the presence of a small electrostatic deflector beyond the magnetic analyzer in beam 2 of this double-beam spectrometer which can also serve as an analyzer itself using the beam optics in reverse. By tuning the magnet to a particular ion, the deflector plate voltage can be scanned and thus the ions which form in the sector (γ- Fig. 2) between the magnetic analyzer and this deflector region can be detected. Despite the low resolution* much useful information can be obtained with this method and any weak but important metastable evidence can be enhanced to detectable levels. Figure 3 shows a typical MIKES trace for the parent peak of bis penta-fluorophenyl thionophosphinyl chloride with the detected daughter ions.

The more recent developments in the realm of defocusing techniques have involved the observation of consecutive metastable transitions. Here, again, Miller has shown[30] how this method can be readily adapted to the AEI-MS 30 instrument to give a direct presentation of these transitions unlike the previous techniques[31,32] which involved indirect analysis and in which the existence of one of the species is only inferred by calculation, not being directly observable. The result has been designated

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* The low resolution can be attributed to several factors. These are discussed in more detail in Ref. 28.

Figure 3
Mikes Spectrum of
m/e 432
for $(C_6F_5)_2P(S)Cl$

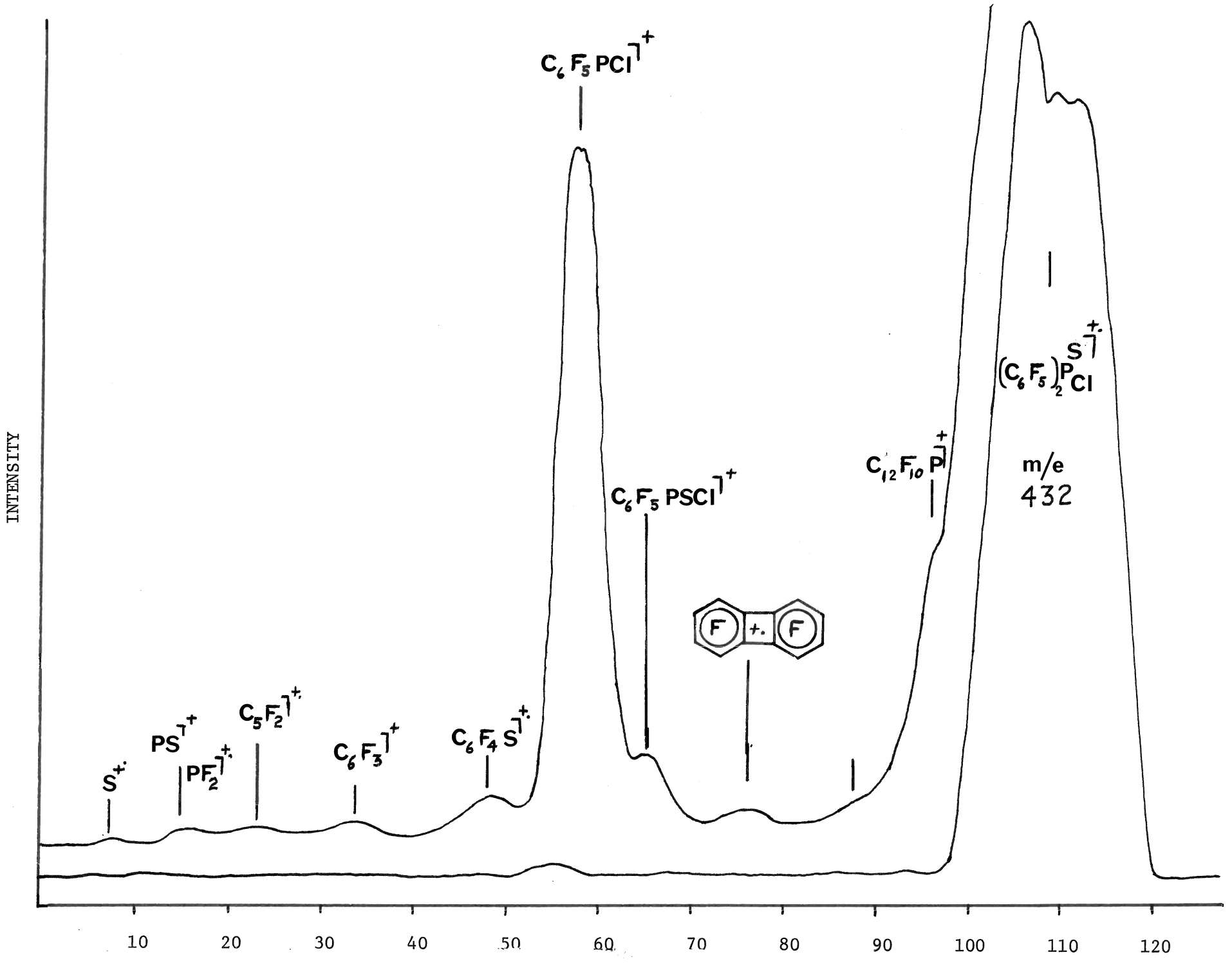
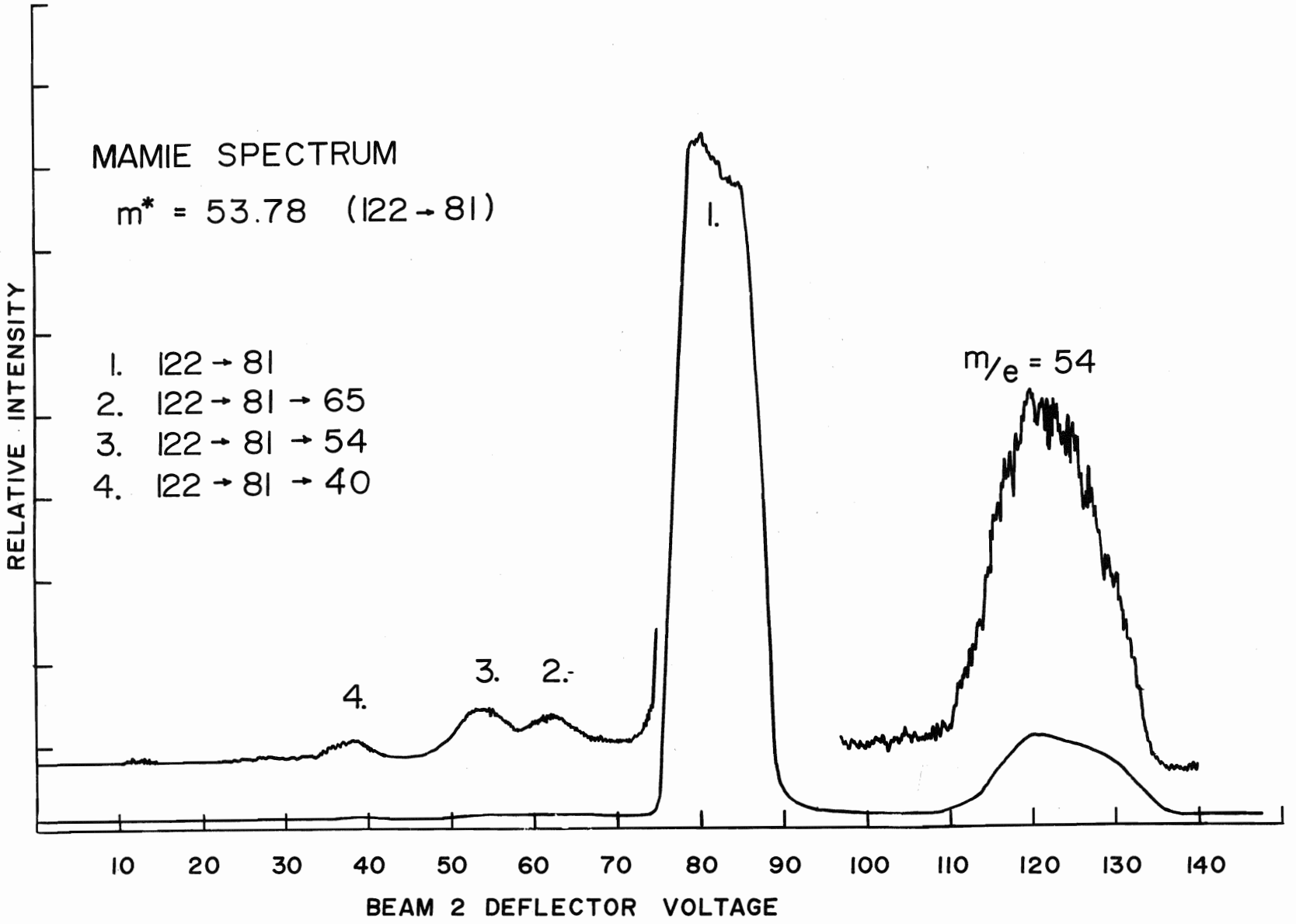

$C_6F_5PCl^+$
$C_6F_5PSCl^+$
$C_{12}F_{10}P^+$
$(C_6F_5)_2PCl$
$S^{+\cdot}$
m/e
432
$S^{+\cdot}$
PS^+
$PF_2^{+\cdot}$
$C_5F_2^{+\cdot}$
$C_6F_3^+$
$C_6F_4S^{+\cdot}$
F
+.
F
INTENSITY
10
20
30
40
50
60
70
80
90
100
110
120
BEAM 2 DEFLECTOR VOLTAGE

Figure 4
MAMIES Trace for
N-trimethylborazole


MAMIE SPECTRUM
m* = 53.78 (122 → 81)
1. 122 → 81
2. 122 → 81 → 65
3. 122 → 81 → 54
4. 122 → 81 → 40
1.
2.
3.
4.
m/e = 54
RELATIVE INTENSITY
10 20 30 40 50 60 70 80 90 100 110 120 130 140
BEAM 2 DEFLECTOR VOLTAGE

as metastable ions arising from metastable ions in ion energy spectra or MAMIES a suitable title in light of the previously described DADI technique. Implementation of this procedure is effected by focusing a normal β-region (see Fig. 2) metastable at the collector. A deflector plate voltage scan will thus give rise to the normal metastable transition as well as peaks corresponding to further decomposition of the metastable daughter ions in the γ-region. A sample presentation is given in Figure 4 where the MAMIES scan is shown for m/e = 53.78 corresponding to the 122 → 81 transition in N-trimethylborazole.

Unstable Organometallic Intermediates and the Synthesis of Polyhaloaromatic Compounds

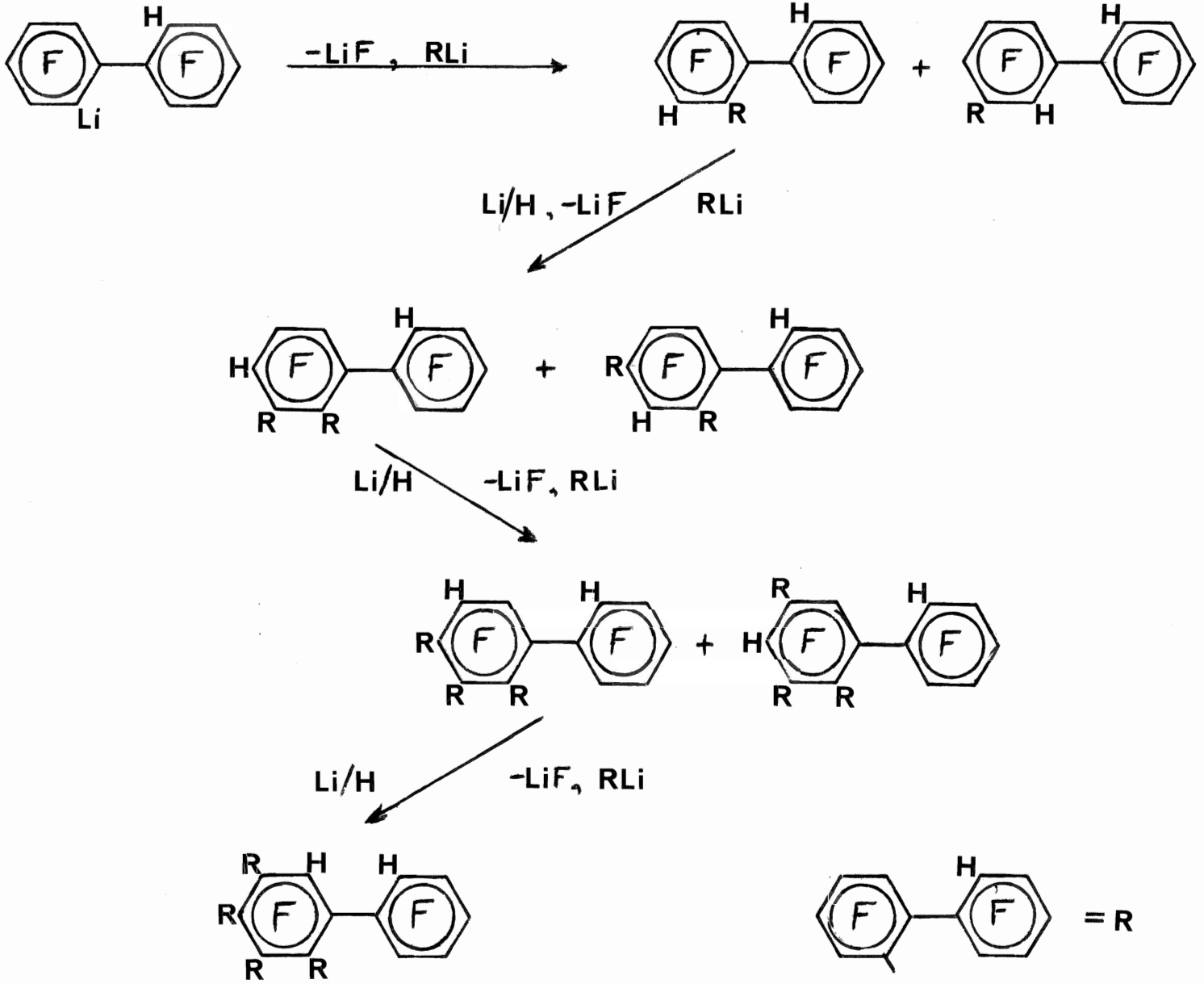
Coe, Stephens and Tatlow[33] were the first to study the generation of benzyne species during the decomposition of pentafluorophenyl lithium and soon afterwards this aspect was exploited by Fenton et al.[34] in the synthesis of 2-substituted nonafluorobiphenyls. In their search for other unstable species which could prove synthetically useful, Cohen et al.[35] obtained good yields (~70%) of a variety of perfluoro biphenyls by slow decomposition of an unstable pentafluorophenyl titanium species. They did not initially provide a hypothetical mechanism for this reaction but in later work[36] studies on $TiCl_4/C_6F_5Li$ ratios showed that no decafluorobiphenyl was obtained for a ratio of less than 1/4. At this latter ratio, formation of $(C_6F_5)_4Ti$ was

suspected and no decafluorobiphenyl was detected. As the ratio increased, optimum yields of the biphenyl were obtained for $TiCl_4/C_6F_5Li$ of 1.5 - 2.0/1, suggesting that the intermediate responsible was $Ti(C_6F_5)_2Cl_2$. Cohen and Massey suggest that this latter species is capable of disproportionation to give decafluorobiphenyl and $TiCl_2$ which could then be oxidized by $TiCl_4$ to $TiCl_3$. There has been no specific attempt to isolate the titanium species responsible or any spectroscopic evidence to suggest the postulated structures.

The results of this coupling reaction have been extended to a variety of synthetic problems, the most important of which have involved the preparation of 2,2'-disubstituted octafluorobiphenyls[36] and a variety of heterocyclic systems involving derivatives of Group IV,[36,37] Group V[38], Group VI[37,39] and the transition metals[36,40].

An effort has been made by a number of workers[33,47] to explain the formation of side products in these systems employing pentafluorophenyl lithium and its derivatives. The formation of a variety of perfluoroaromatics has been ascribed to the formation of benzyne we mentioned previously and it has been shown that products arising in this system can be ascribed to up to five consecutive nucleophilic addition/benzyne formation sequences as depicted in Figure 5. Elimination of these side products seems impossible but they can normally be removed fairly easily from the desired products.

Figure 5
Side Reactions of
Perfluoroaryl Lithium
Species


-LiF , RLi
Li/H , -LiF
RLi
Li/H
-LiF, RLi
Li/H
-LiF, RLi
= R

Synthesis and Mass Spectra of Dibenzophospholes

The first example of a phosphole system (general form Fig. 6a), 5-phenyl dibenzo phosphole* (Fig. 6b) was isolated by Wittig and Geisler in 1953[42]. Though phosphole (Fig. 6a, X = H) itself has not yet been synthesized a large number of compounds of this system have been prepared in the intervening years and most of these are catalogued in a comprehensive review by Hughes and Srivanavit[43]. As one might suspect, with the growth in this field, a multitude of synthetic routes have developed and in Figure 7 four of the most important pathways to a 5-phenyl dibenzophosphole are indicated. Of these routes A and B have proven to be most useful and given to higher overall yields (60%+).

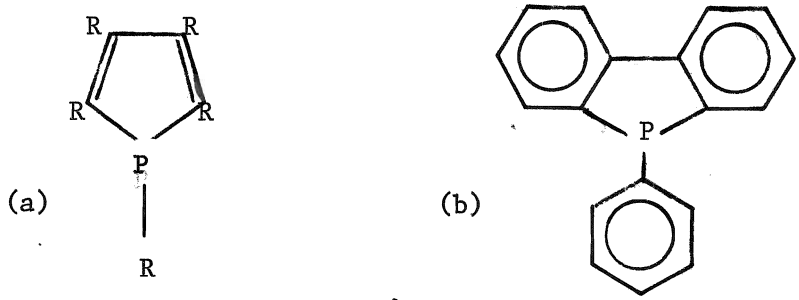


Fig. 6

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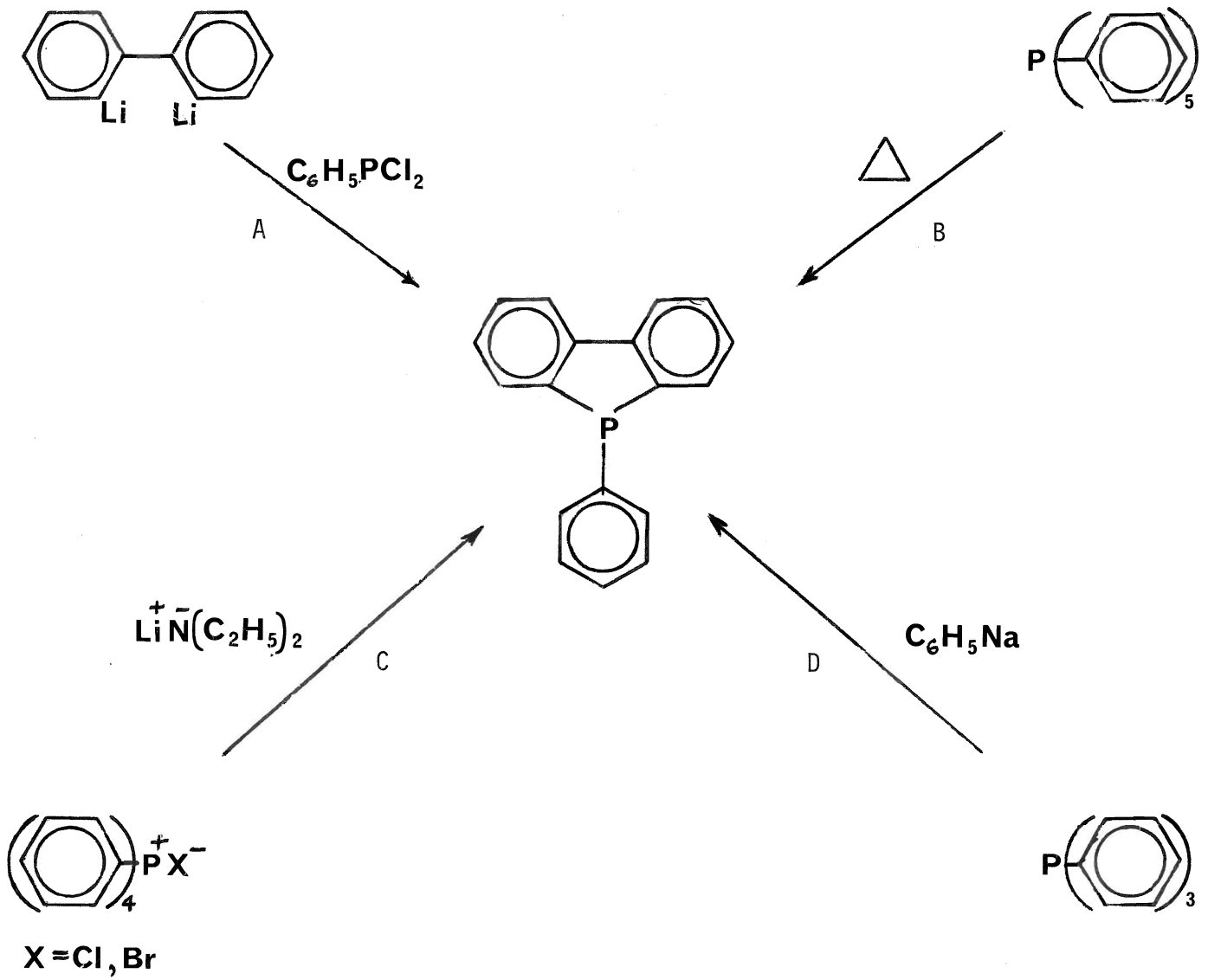
* The nomenclature of this system was originally designated as 9(phenyl) phosphafluorene with the numbering of the ring system as indicated (I).

This was consistent with the related system but has been discarded in favour of the numbering scheme depicted in (II) which has been used in describing these as 5-substituted dibenzo metalloles.

Figure 7
Common Methods Used
in the Synthesis of
5-phenyl dibenzophosphole


Li Li
$C_6H_5PCl_2$
A
B
P 5
P
$Li^+\bar{N}(C_2H_5)_2$
C
D
C_6H_5Na
P^+X^- 4
P 3
X = Cl, Br

The main concern with most extensions of the phosphole unit is centered around the possible aromaticity of these compounds. Quin et al.[48] have completed a detailed study of 1-methyl phosphole in this respect and offer substantial evidence to suggest delocalization of electron density in this molecule. Part of their evidence happens to have been the mass spectrum of this compound, reported in some detail and being the first published on this type of system. Despite the supporting arguments, 1-methyl phosphole and all other phospholes (including the dibenzo phospholes) reported to date undergo the normal reactions of tertiary phosphines, i.e. formation of oxide, sulfide, selenide and tertiary salt and for this critical reason have not been claimed to be aromatic.

The sole example of an octafluoro-dibenzophosphole was the 5-phenyl derivative prepared by Chambers and Spring[38] using a method similar to A in Fig. 7. In addition they reported the corresponding phosphole oxide and a number of products resulting from nucleophilic substitution on the fluoro-aromatic ring system. There has been no apparent interest in other 5-substituted derivatives of this system.

The available mass spectral data on dibenzophospholes is meager indeed, the only published work being studies by Hellwinkel et al.[62] on a variety of Group V dibenzo heterocyclics though we have previously investigated some of these in our own laboratory. Clearly, the whole field of phosphole

derivatives provides a challenging area of research and studies in their mass spectra can only supplement the data needed to determine the relative aromaticity of these compounds.

EXPERIMENTAL

(1) General Techniques

All reactions involving organolithium reagents were performed in apparatus which had been baked overnight in an oven and finally purged with dry nitrogen while being flamed. Melting points were taken using a Kofler Hot-Stage apparatus. Column chromatography involved the use of either neutral alumina (Brockmann Grade 1) or Florisil (80/100 mesh) with 30/60 petroleum ether as the normal eluant. Micro analyses were performed by Dr. E. Pascher (Mikro-analytisches Laboratorium, Buschstr, 54, 5300 Bonn, West Germany).

n-Butyl lithium was titrated* regularly using procedures described by Gilman et al.[50,51] to check for fluctuations in concentration.

(2) Purification of Reagents

Tetrahydrofuran was pre-dried over potassium hydroxide followed by distillation from either lithium aluminum hydride or calcium hydride. All other solvents were dried and distilled by appropriate methods where necessary. Reagents obtained from suppliers are listed in Table 1.

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* For each titration 3 aliquots of 1 ml. of n BuLi solution in 10 ml distilled water were titrated with standard acid to a phenophthalein endpoint. Results were reproducible within ± 1%. A more elaborate method of analysis has also been described by Collins et al. 52.

Compounds generously provided by Professors M. Fild, M.D. Rausch and D.W. Meek are shown in Table 2. All compounds used in mass spectral studies were purified where necessary* by fractional distillation (for liquids) or recrystallization and vacuum sublimation (for solids).

(3) Instrumentation

Infra-red spectra were taken using a Perkin Elmer 237B Grating Infrared Spectrophotometer and potassium bromide pellets of each compound studied. Relevant proton N.M.R. data was obtained on a Varian A-60 NMR spectrometer. Gas chromatographic analysis were performed on either a Varian Aerograph 90P3 gas chromatograph (for simple analysis) or a Pye-Unicam 104 chromatograph interfaced on an AEI-MS 30 mass spectrometer for combined GC/MS work. A column (6' X ¼") of 3% SE30 on chromosorb w was used exclusively for all GC runs. It should be noted at this stage that all the gas chromatographic analysis referred to in this work are strictly qualitative since it was not to the point of this study to perform quantitative measurements on the systems involved.

All mass spectral studies were done using an AEI MS-30 double beam, double focusing mass spectrometer using the solid introduction probe for solid samples and either the

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* Compounds from external sources were checked for impurities by MS or GC/MS techniques before use.

TABLE 1

REAGENTS

	Compound	Formula	Supplier
1.	Titanium Tetrachloride	$TiCl_4$	Fischer Scientific, Fairlawn, N.J.
2.	Phosphorous Trichloride	PCl_3	Mallinckrodt Chemical Works, St.Louis, Mo.
3.	Phosphorus Pentachloride	PCl_5	Matheson, Coleman-Bell, Norwood, Ohio
4.	Phenyldichlorophosphine	$C_6H_5PCl_2$	Alfa-Ventron, Beverly, Mass.
5.	n-Butyl lithium	C_4H_9Li	Alfa-Ventron, Beverly, Mass. (2.4 or 2.0M solution in nepane)
6.	Methyl lithium	CH_3Li	Alfa-Ventron, Beverly, Mass. (1.8M solution in ether)
7.	Pentafluorobenzene	C_6F_5H	Fluorochem Ltd., Dinting Vale Trading Estate, England.
8.	Bromo pentafluorobenzene	C_6F_5Br	Pierce Chemical Co., Rockford, Illinois
9.	1,2 dihydrotetrafluoro benzene	$C_6F_4H_2$	Columbia Organic Chem. Co. Inc., Columbia, S.Carolina.
10.	1,3,5 trimethyl benzene	C_9H_{12}	Eastman Org. Chem., Rochester, N.Y.
11.	Pentafluoroaniline	$C_6F_5NH_2$	Pierce Chemical Co., Rockford, Illinois.

TABLE 2

COMPOUNDS FROM OUTSIDE SOURCES

Compound	Supplier
Group A	
$C_6H_5PSF_2$	M. Fild Lehrstukl B. fur Anorganische Chemie der Technischen Universitat Braunschweig * For preparations see Ref. 72
$C_6H_5PSCl_2$	
$C_6F_5PSF_2$	
$C_6F_5PSCl_2$	
$C_6F_5PSBn_2$	
$C_6F_5(CH_3)PSF$	
$C_6F_5(C_2H_5)PSF$	
$C_6F_5(t\text{-}C_4H_9)PSF$	
$C_6F_5(C_6H_5)PSF$	
$C_6F_5(C_6F_5)PSF$	
$C_6F_5(C_6F_5)PSCl$	
$C_6H_5(C_6H_5)POF$	
$C_6F_5(C_6H_5)POF$	
$C_6F_5(C_4H_9)POF$	
$(C_6F_5)_3PF_2$	
Group B	
$C_6F_5P(CH_3)_2$	D.W. Meek, Ohio State University, Akron, Ohio. ** For preparation see Ref. 82
$C_6F_5As(CH_3)_2$	
$C_6F_5PO(CH_3)_2$	
$C_6F_5PS(CH_3)_2$	
$C_6F_5PSe(CH_3)_2$	
Group C	
$(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2$	M. Rausch, University of Massachusetts, Amherst, Mass. *** For preparations see Ref. 22
$(C_{12}F_8)Co(\pi\text{-}C_5H_5)CO$	
$(C_{12}F_8)Rh(\pi\text{-}C_5H_5)CO$	
$(C_{12}F_8)Ir(\pi\text{-}C_5H_5)CO$	

AGHIS (All Glass Heated Inlet System) or gas chromatograph inlet system for liquids, and with an ionization voltage of 70eV, a resolution of ca. 1000 and a 4KV accelerating voltage. "MIKES" and "MAMIES" spectra were recorded by methods previously described[28,30]. Metastable transitions were assigned with the aid of a FORTRAN computer program BMETAST which fits the observed metastables to the peaks in the spectrum. Isotopic patterns for particular ions were calculated using the FORTRAN program BMASROS while relative abundances of overlapping isotopic multiplets were computed by a least squares fit of the output of BMASROS to the observed spectrum using the Fortran program BMASABD. All computations were carried out on a B5500 computer.

(4) Preparation of 2,2' Dihydro octafluorobiphenyl

(a) The basic procedure of Cohen et al.[35] was followed and the product was isolated in good yields (65-85%) and purified by vacuum sublimation (70-80°C) M.P. 80-81°C. (Lit.[35] 79-80°C)

(b) Rapid Decomposition

1,2,3,4 tetrafluorobenzene (6.0g, 40 mmole) in 50 ml. THF at -78°C was treated with n-BuLi (20.0 ml. of a hexane solution (40 mmole)). After 30 minutes stirring 10.0 ml (ca 91 mmole) $TiCl_4$ was added but instead of the normal slow decomposition procedure, the reaction mixture was allowed to come to room temperature over a

two-hour period. The solution was hydrolysed with dilute hydrochloric acid and the ether layer separated, dried ($MgSO_4$) and evaporated to give an orange-brown oil which was chromatographed on Florisil (80/100 mesh) and eluted with 30/60 petroleum ether. The first fraction eluted was 2,2' dihydrooctafluorobiphenyl (2.16g, 36.2% of theoretical yeild). Further elution with 50:50 petroleum/ethyl ether and 80:20 ethyl ether/acetone brought down fractions A & B two red-brown oils (ca. 1.5g and 0.8g respectively) which were analyzed by G.C./M.S. The results of the analysis are shown in Table 3. A black, resinous material remained on the column and this was not investigated further. A second run of this sequence gave very similar results (see Table 3 for details).

(5) Preparation of 2,2' Diiodooctafluorobiphenyl.

The reported procedure[36] was followed and the product was isolated in yields of 80-85% as (after sublimation $80^{o}C/10^{-2}mm$) faint yellow crystals MP 80-81°C (LIT[36] 80-82°C).

(6) Preparation of 5-substituted octafluorodibenzophospholes

(a) Method A

Addition of appropriate phosphorous dichloride derivative ($RPCl_2$) to 2,2' dilithiooctafluorobiphenyl.

The procedure used was basically the same as described in the literature[38]. The orange oils which always

TABLE 3

RESULTS OF GC/MS RUNS ON RAPID DECOMPOSITION PRODUCTS OF $TiCl_4/C_6HF_4Li$

Sample	Peak	Retention Time (min.)	m/e	Assignment
A	1	3.0	220	---
	2	3.5	298	$C_{12}F_8H_2$
	3	9.7	446	$C_{18}F_{12}H_2$
	4	10.6	428	$C_{18}F_{11}H_3$
	5	11.0	410	$C_{18}F_{10}H_4$
	6	11.9	428	$C_{18}F_{11}H_3$
	7	12.4	516	$C_{24}F_{12}$
	8	13.1	542	$C_{24}F_{13}H_7$
	9	13.8	560	$C_{24}F_{14}H_6$
B	1	4.0	298	$C_{12}F_8H_2$
	2	9.3	322	---
	3	10.0	314	$C_{12}F_8HOH$
	4	10.8	354	$C_{18}F_7H_5$
	5	11.0	290	---
	6	11.4	352	$C_{18}F_7H_3$
	7	11.9	428	$C_{18}F_{11}H_3$
	8	12.6	522	$C_{24}F_{12}H_6$

resulted from the organic extractions were chromatographed on neutral alumina and the phospholes were eluted in the first fraction as white solids*. A summary of the preparations using this method are given in Table 4.

(b) Method B

Addition of the appropriate organometallic (RMgX or RLi) to 5-chlorooctafluorodibenzophosphole (prepared in situ) 2,2'-dihydrooctafluorobiphenyl (1.49g/5 mmole) in 10 ml. THF at -78°C was treated with 5.10 ml (10.2 mmole) n-Bu Li/Hexane and the mixture was stirred at this temperature for 3 hours. Phosphorous trichloride (0.69g/5 mmole) in 5 ml. THF was added dropwise over a 5-minute period and stirring was continued for 2 hours, while the mixture warmed to -10°C. The solution was transferred under nitrogen to a 250 ml flask and a filtered solution of C_6F_5MgBr (5 mmole) (from 1.24g C_6F_5Br and 0.12g Mg) in 30 ml ether was added over 15 minutes at 0°C. After the addition was complete, the mixture was stirred overnight and then refluxed for 2 hours. The mixture was hydrolyzed with dilute sulfuric acid, separated, and the ether layer dried

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* The reaction involving $C_6F_5PCl_2$ gave rise to a brown oil as the first band from the column. GC/MS showed the sample contained 4 major components corresponding to $C_{12}F_8H_2$, $C_{18}F_{15}P$, $C_{16}F_8H_9P$ and $C_{18}F_{13}P$ (desired product).

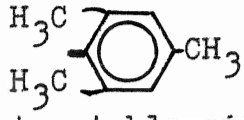
($CaCl_2$) and evaporated. The resulting brown oil was chromatographed on neutral alumina and elution with light petroleum brought down a yellow oil which crystallized to give 0.15g of $C_{12}F_8PC_6F_5$ (identified by mass spectrum). The compound was recrystallized from ethanol to give ca 85 mg. of white needles (mp. 151-153°C. Repetition of this method on larger scales for R = $-CH_3$, $-C_6F_5$,  (ca. 50 mmole quantities) gave rise to intractable oily tars in all three cases. GC/MS analysis of these materials indicated the presence of the required phosphole in the first two cases along with the typical conglomeration of fluoroaromatics. In the case of the mesityl derivative, the phosphole could not be detected, the major components being mesitylene and 2,2' dihydro-octafluoro-biphenyl. Since no mesityl bromide could be detected, it appears that the Grignard did not attack the intermediate phosphole chloride (perhaps as a result of steric influences). Attempts to separate and purify these phospholes by repeated chromatography and/or sublimation were unsuccessful. Small portions of these mixtures were treated with methyl iodide in the hope of isolating the quaternary salts but none were isolated.

TABLE 4

SUMMARY OF PHOSPHOLE/METALLOLE PREPARATIONS

Compound	Method	M.P.	% Yield	Analysis
$C_{12}F_8PC_6H_5$	A	123-4°C	65-75%	Found: C,53.22; F 37.90; P7.66 H 1.12. Calc: C 53.49; F 37.60; P 7.66; H 1.25%
$C_{12}F_8PC_4H_9$	A	121-23°C	68%	Found: C 50.00% F 39.77; P 7.80; H 2.40. Calc: C 50.02%; F 39.56%; P 8.06%; H 2.36%
$C_{12}F_8PC_6F_5$	B	151-53°C	3 - 5%	--------
$C_{12}F_8PCH_3$	B	--------	~3 - 8%*	--------
$C_{12}F_8Ti(\pi\text{-}C_5H_5)_2$	A	dec (~250°C)	~10%	--------

* Estimated from GC/M.S. and G.C. data.

(d) The reaction of 2,2' dilithiooctafluorobiphenyl with PCl_5.

$C_{12}F_8Li_2$ (1.1 mmole) was prepared from 2,2' diiodooctafluorobiphenyl (0.62g/1.1 mmole) and 1.2 ml. n BuLi/hexane (2.4 mmole) at -78°C in 25 ml. THF under nitrogen and the solution of $C_{12}F_8Li_2$ was added over 15 min. at -78°C. When the addition was complete, the mixture was allowed to come to room temperature and stirred for 2 hours. The pale yellow slurry of PCl_5/THF turned light green and gradually became orange-brown as the temperature returned to 25°C. The precipitated solid was filtered under nitrogen and mass spectral analysis indicated some PCl_5 was still present. The resulting mixture was hydrolyzed with dilute sulfuric acid and the ether layer separated, dried and concentrated to give a red-orange oil which was analyzed by GC/MS (for results see Table 5). By far, the major component was found to be 2,2'-dihydro-octafluorobiphenyl, suggesting that a very limited amount of reaction had occurred between $C_{12}F_8Li_2$ and the PCl_5.

(e) Attempted Isolation of 5-chlorooctafluorodibenzophosphole

Doak et al.[53] had isolated 5-chloro dibenzophosphole in low yield by cyclo-dehydrohalogenation of 2-biphenyldichlorophosphine. 2,2' dilithiooctafluorobiphenyl was prepared in the usual way at -78°C (2.75g/5 mmole $C_{12}F_8I_2$ and 5.10 ml/10.2 mmole n BuLi/hexane). PCl_3

TABLE 5

G.C./M.S. ANALYSIS OF $C_{12}F_8Li_2$
REACTIONS WITH
(a) PCl_3
(b) PCl_5

Sample	Peak	Retention Time (Min.)	m/e	Assignment
(a)	1	1.3	298	$C_{12}F_8H_2$
	2	2.0	354	$C_{12}F_8POH$
	3	2.6	328	$C_{12}F_8PH$
	4	4.1	480	$C_{24}F_{10}H_2$
	5	4.5	424	$C_{12}F_8HI$
	6	16.0	550	$C_{12}F_8I_2$
	7	18.0	624	$C_{24}F_{11}I$
(b)	1	5.7	298	$C_{12}F_8H_2$
	2	9.0	532	$C_{12}F_7HI_2$

(0.69g/5 mmole) was added over 10 minutes and the deep blue-violet colour gradually faded to bright orange as the mixture was subsequently allowed to come to room temperature. The solvents were pumped off and the residue dissolved in benzene and treated with hexane. The resulting solution was siphoned off from a waxy residue. (MS analysis of the latter indicated the presence of polyfluoro aromatics already seen in other reactions). The benzene solution was analyzed by G.C./M.S. (see Table 5).

(7) Preparation of Organometallic Derivatives

(a) 5,5 di(π-cyclopentadienyl) octafluorodibenzotitanole

This compound was prepared by a similar procedure to that described by Cohen and Massey[36] with some slight revisions.

$C_{12}F_8H_2$ (2.50g/9 mmole) was treated with n-BuLi (9.05 ml/ 18.1 mmole) at -78°C in 50 ml. THF. After 3 hours stirring, di- π cyclopentadienyl titanium dichloride (2.12g/9 mmole) in 100 ml. THF was added over 30 minutes and the mixture allowed to come to room temperature. The solvent was stripped off and the dark residue was washed with hot pet-ether and then extracted with hot benzene. Concentration of the benzene solution and treatment with pet-ether gave 0.63g of an orange solid (14.8% theoretical). Attempts were made to recrystallize

the material from benzene/pet ether mixtures but a crystalline product could not be obtained. The material (recrystallized) charred and decomposed at ca 250°C, (0.42g/9.9%). Structure confirmed by mass spectrum. (M^+- m/e 474)

(b) Attempted Preparation of 5.5' dicyclopentadienyl octafluorodibenzozirconole

The preparation described for the titanium analog was followed explicitly using equimolar quantities of $C_{12}F_8Li_2$ and $(\pi\text{-}C_5H_5)_2\ ZrCl_2$ (2.34 g/8 mmole). No prepicitate could be isolated from the benzene extract and analysis (GC/MS) of the residue showed only starting materials and polymeric species were present. Rausch et al.[40] describe the isolation of this species and report it to be much more susceptible to hydrolysis than the corresponding titanium or hafnium derivatives. (A sample sealed under nitrogen slowly decomposed at room temperature to give octafluorobiphenyl.) Similarly, a sample of the corresponding Hafnole received for mass spectral analysis had decomposed to 2,2' dihydrooctafluorobiphenyl.

(8) Preparation of Miscellaneous Reagents

(a) Phosphonous Dichlorides ($RPCl_2$)

(i) R = C_6F_5

Prepared as described by Miller[54] or Magnelli[55] et al. by addition of filtered solution of C_6F_5MgBr to

PCl_3 at c. -50°C and distillation of the resulting mixture after 3 hours at room temperature. The product bp. 75-79°C/20 mm. was refractionated but the mass spectrum indicated some C_6F_5PClBr and $PBrCl_2$ were present (in small amounts).

(ii) R = $t\text{-}C_4H_9$

Prepared as by Metzger et al.[56] by addition of $t\text{-}C_4H_9MgBr$ to PCl_3 at ca - 50°C and fractionation of the resulting mixture. Product boiled at 145-155°C under nitrogen and was pure by MS analysis.

(iii) R = CH_3

This attempted preparation has not been described in the literature using either CH_3MgI or CH_3Li. The only organometallic used in this synthesis has been $Pb(CH_3)_4$[57]. Despite using excess PCl_3 and low temperatures (-78°C), a decent yield of CH_3PCl_2 could not be obtained. The fraction collected always boiled above 80°C but consistently contained gross impurities of PCl_3 and $(CH_3)_2PCl$.*

(iv) R = 2,4,6 $(CH_3)_3$ (C_6H_2)

Preparation of mesityl phosphonous dichloride was attempted by both alkylation of PCl_3[59] and reaction of $C_9H_{11}MgBr$ with PCl_3. A sufficiently pure

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* Boiling Ranges[80]:

PCl_3	- 75-76°C
CH_3PCl_2	- 81-82°C
$(CH_3)_2PCl$	- 72-75°C

material could not be obtained in either case as $C_9H_{11}PBrCl$ and mesitylene were still present after several distillations. A recent amendment to the latter route has been made by Brazier et al.[60], using $ZnCl_2$ in the Grignard mixture.

(b) $C_6F_5N(CH_3)_2$

The above compound was prepared from $C_6F_5NH_2$ by the method of Allen et al.[58] and the product had a boiling range of 158-161°C and was pure by G.C. and G.C./M.S. analysis.

(9) Thermolysis Studies on Thiono phosphonyl & Thiono-phophinyl Halides.

The tests described here are related to some rather astounding rearrangements described in later sections.

(a) Pyrolysis

2.0 ml samples of each of the compounds listed below were sealed in melting-point capillaries under nitrogen and heated in a melting point apparatus at 150°C for 30 minutes. Mass spectra were run immediately after heating.

(b) Low-Temperature Spectra

The spectra of the relevant compounds were taken at a source temperature of 50°C.

(c) Compounds Tested:

(i) $(C_6F_5)_2PSCl$

(ii) $(C_6F_5)(C_6H_5)PSF$

(iii) $(C_6F_5PSCl_2$

(iv) $(C_6F_5)(C_2H_5)PSF$

The spectra of these compounds taken under the conditions outlined in (a) and (b) were identical with those obtained under normal operating conditions showing none of the effects one would have expected from a molecular rearrangement, the most notable of which would have been a severe depression of the molecular ion abundance similar to the low abundance observed for pentafluorothiophenol derivatives of Group IV(81).

RESULTS AND DISCUSSION

1. General Features of the Mass Spectra of Some Phosphine Derivatives.

The mass spectra referred to in this section are shown in Figures 9-13, 15-20, 22-25, 27 and 28, being grouped according to the following classifications:

(A) Thionophosphonyl halides ($RPSX_2$)

(B) Thionophosphinyl halides (RR^1PSX)

(C) Phosphinyl halides (RR^1POX)

(D) Miscellaneous Species

(i) Tris (pentafluorophenyl) phosphorous difluoride

(ii) Ethyl bis (pentafluorophenyl) phosphinothioite di fluoride.

The fragmentation schemes for these groups are depicted in Figures 14, 21, 26 and 29 respectively with metastable supported transitions indicated.* Aside from the propensity of the compounds to undergo some rather spectacular rearrangements during the breakdown process, there are some basic patterns which evolve from the spectra. In all cases except that of $(C_6F_5)_2PF_2(SC_2H_5)$ strong molecular ions were observed. A common decomposition pathway involved cleavage of the phosphorous-carbon bond and in the mixed secondary derivatives scission favoured formation of the most stable positive ions. These features seem to be consistent with the limited amount of published data on comparable systems[13, 14, 63-66].

The rearrangements which occurred under electron

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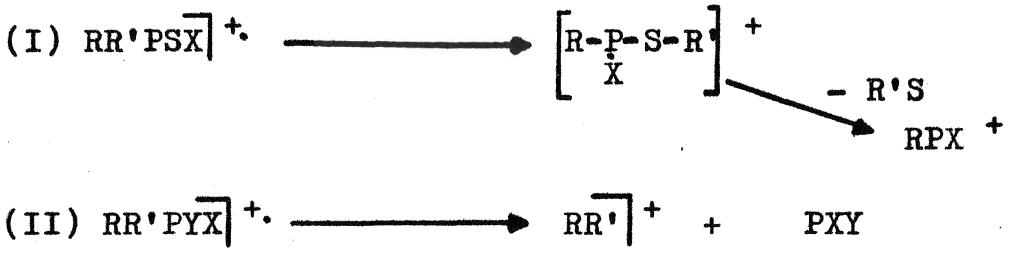
* For detailed metastable data see Appendix A.

impact included the processes depicted below as well as evidence for the operation of halogen-transfer rearrangements



previously observed in other similar fluoroaromatic systems[13, 14].

Process (I) is vaguely related to molecular ion rearrangements observed by Cooks and Gerrard[61] where various substituted phosphoramidothioates (RO)(R'O)(NR_2")P=S, phosphorochloridothioates (RO)(R'O)(X)P=S, and phosphorothioates (RO)(R'O)(R"O)P=S, gave rise to isomerization of the molecular ion to the corresponding thiohalophosphates, ie (RO)(R'S)($NR"_2$)P=O, (RO)(R'S)(X)P=O, and (RO)(R'O)(R"S)P=O respectively. The fact that source temperatures were in the range 50 - 60°C when the spectra were recorded suggests that these rearrangements were induced by electron impact rather than results of thermal influences. It is conceivable that the rearranged species represent lower energy forms even though the molecules are already in excited (ionized) states if one considers the extra stability involved in formation of a phosphoryl (P=O) vs. thiophosphoryl (P=S) bond. In the cases observed in this work there is no motivation

for such molecular changes to occur. All of the species studied having P = S bonds gave evidence for rearranged ions in their spectra, showing a marked tendency towards aryl-sulfur bond formation in systems involving alkyl/aryl substituted phosphorous.

(A) Thiono-phosphonyl halides ($RPSX_2$)

The partial mass spectra of these compounds are summarised in Table 6. For purposes of more effective comparison these will be described further as $C_6X_5PSY_2$ where X = H,F and Y = F,Cl,Br. In all cases, strong parent ions are observed which also represent the most abundant species (except for Y = Br). Changes in X are reflected in a corresponding increase in the abundance of $C_6X_5^+$ for X = H, a rather obvious consequence considering the greater electronegativity of the C_6F_5 group. Indeed, this may serve to explain the increase in the intensity of the $C_6X_5S^+$ species as well.

Looking more carefully at the series X = F, Y = F,Cl,Br one cannot draw any useful correlations from the parent ion abundances although a general decrease in intensity is suggested. The fact that $C_6X_5PY_2S$ is slightly less abundant for Y = Cl than for Y = Br is probably a result of the propensity of the former ion to lose PCl_2 or $PFCl_2$ thus forming C_6F_5S and C_6F_4S respectively (net abundance for these is 12.1 for Y = Cl vs. 1.6 for Y = Br) whereas the bromide favours halogen cleavage to give much more abundant

TABLE 6

PARTIAL MASS SPECTRA OF $C_6X_5PSY_2$

(X = H, F; Y = F, Cl, Br)

Ion+	X = F, Y = F	X = F, Y = Cl	X = F, Y = Br	X = H, Y = F	X = H, Y = Cl
$C_6X_5PY_2S$	28.4	14.1	15.9	19.3	46.6
C_6X_5PYS	1.2	6.1	33.8	0.5	26.9
$C_6X_5PY_2$	1.7	3.3	0.8	1.0	0.5
C_6X_5PY	---	4.0	3.3	2.0	4.4
C_6X_5PS	---	1.6	12.2	---	0.5
PY_2	31.3	13.7	6.3	4.2	---
C_6X_5S	8.0	2.2	---	18.5	6.4
C_6X_4S	3.6	9.9	1.6	---	---
C_6X_5	0.9	0.4	---	8.0	3.1
PS	0.6	4.4	8.2	1.8	1.0
PXY	(See PY_2)	4.0	1.1	---	---
C_6X_4	4.9	0.9	1.8	1.6	---
C_6X_3	0.4	---	---	1.5	---
C_5X_4	0.3	---	---	2.8	---
C_5X_3	2.2	2.6	1.1	---	---
C_4X_3	0.4	1.7	---	8.2	---
C_5X_2	1.0	---	0.5	---	---
C_3X_3	1.4	1.2	0.5	---	---

M-Y and M-2Y ions (comparative abundance (M-Y: Y = Cl, 6.1; Y = Br, 33.8; (M-2Y): Y = Cl, 1.6; Y = Br, 12.2). The anomalous behaviour for Y = F can be rationalized in terms of a greater tendency towards loss of C_6F_5S to give the PF_2 ion in very high abundance thus following the basic behaviour of the chloride while minimizing fragmentation by the sequential halide loss seen in the bromide.

These observations suggest that experiments on the perchlorophenylthionophosphonyl dichlorides may serve to prove whether PCl_2+ formation would be favoured under similar circumstances.

In the hydrocarbon series (X = H, Y = F,Cl) it is clear that the initial loss of PF_2 is still most important for Y = F but now, as we have said earlier, the charged species are represented by the ring residues, the PF_2 abundance being much lower. This variance is demonstrated most effectively by the ions C_6X_5S (X = F, 8.0%; X = H, 18.5% and C_6X_5 (X = F, 0.9%; X = H, 8.0%). The high abundance of the M and (M-Y) ions for Y = Cl dominate the spectrum to such an extent (net abundance 73.5%) that very few fragments are formed; indeed the normal aromatic ion series of m/e 51, 50, 26, 25 is quite negligible. The complete absence of a PCl_2+ ion suggests that the rearrangement which results in the formation of $C_6H_5S^+$ probably involves initial P-S-C_6H_5 bond formation before decomposition, the positive charge being delocalized thoroughly into the thio phenol system.

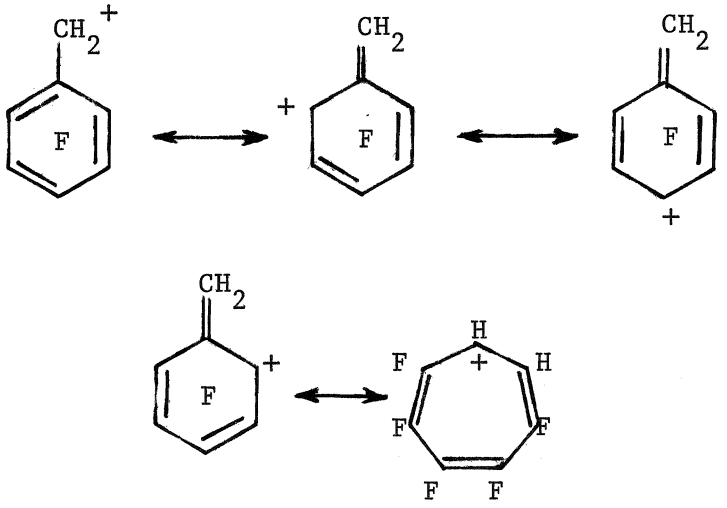
away from the electronegative chlorine atoms. It logically follows that one would expect a similar decrease in PF_2^+ abundance for Y = F and as was already noted, this is the observed pattern.

It is clear from the data presented in the table that halogen transfers are occurring from the aromatic ring in the X = F compounds, the mixed PXY ions demonstrating this facet most effectively.

(B) Pentafluorophenylthionophosphinyl Halides (C_6F_5RPSX)

The partial mass spectra of these compounds are summarized in Table 7. For alkyl R, the abundance of the parent ions follows the series $CH_3 > C_2H_5 >> t.C_4H_9$. The slight lowering due to the C_2H_5 group can be attributed to the competitive breakdown process involving loss of ethylene while the gross difference for $t\text{-}C_4H_9$ can be explained in terms of the stable tertiary butyl cation which is the most important fragment in this spectrum carrying almost 70% of the total ion current. It is noteworthy that the table does not indicate the wide variety of ions formed by $C_6F_5\text{-}R$ interactions. For example, in the spectra where R is aromatic, a number of biphenylene type ions of the form $C_{12}F_4X_4$(X = H,F) are detected while in the R = alkyl spectra an ion at m/e 181 corresponding to $C_7F_5H_2$ is present and its abundance follows the expected series, $CH_3 > C_2H_5 > t\text{-}C_4H_9$. We will not discuss the rearrangement resulting in the forma-

tion of this ion (I) but suffice it to say that such tropyllium-like ions are well known as major species in the mass spectra of alkyl substituted benzenes.



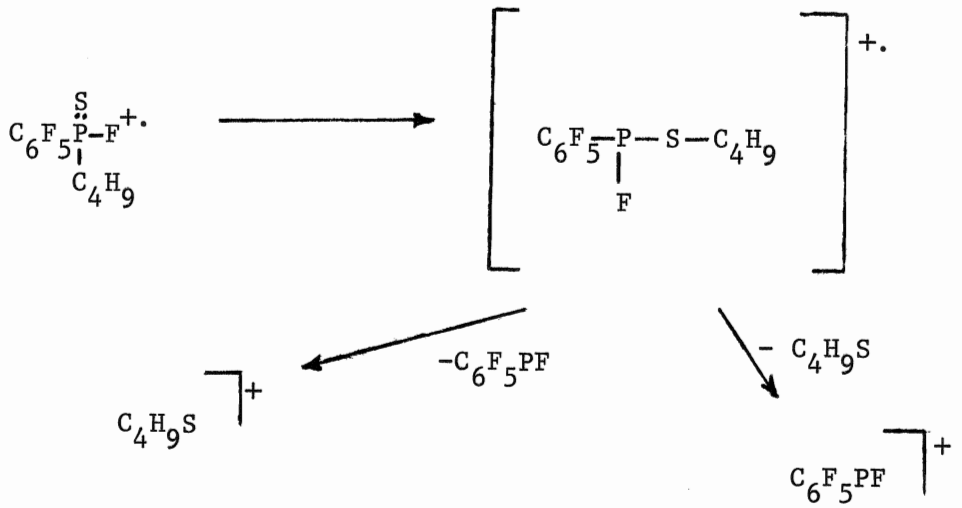
The most notable feature of the spectra for R = aromatic is the appearance of strong ions corresponding to the species RPX. Metastable ion data shows that these arise directly from the parent ions by loss of a C_6F_5S radical species. The implications are, of course, that the molecule rearranges to the thioester before breakdown. It is interesting to note that in the mixed compound, $(C_6H_5)(C_6F_5)$ PSF, rearrangement to C_6F_5S is almost exclusive (Abundance of residual species 32.4%/C_6H_5PF vs 1.8%/C_6F_5PF) suggesting that the rearrangement is somewhat selective, giving rise to the more stable cation. Returning to the alkyl substituted moieties, the case of R = CH_3 is the only one devoid of fiercely competitive fragmentation modes and the abun-

TABLE 7

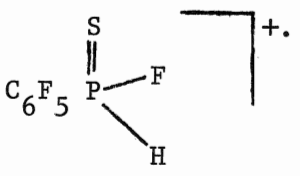
PARTIAL MASS SPECTRA FOR C_6F_5RPSX

Ion$^+$ R = X =	CH_3 F	C_2H_3 F	t-C_4H_9 F	C_6H_5 F	C_6F_5 F	C_6F_5 Cl
C_6F_5RPSX	16.3	15.4	2.3	7.8	19.2	13.2
C_6F_5RPS	---	---	---	0.6	6.9	7.0
C_6F_5RPX	1.3	1.0	0.2	---	1.4	1.3
C_6F_5RP	---	---	---	---	0.7	1.2
RC_6F_4S	0.9	---	---	---	1.9	1.3
C_6F_5PSX	3.6	2.1	0.6	0.1	6.5	2.9
RPSX	2.8	1.1	---	1.6	---	---
C_6F_5PX	3.9	19.8	1.9	1.8	40.1	21.1
RPX	9.4	2.0	---	32.4	--C_6F_5PX--	
PF_2	9.2	9.9	4.4	3.2	4.7	7.9
PS	1.4	1.8	---	1.2	0.4	4.6
C_6F_5S	0.4	---	---	0.2	1.4	1.2
C_6F_4S	4.3	4.1	0.7	0.7	2.8	2.2
C_6F_3S	0.9	---	---	---	0.3	---
C_6F_5	0.4	---	---	0.3	0.2	0.3
C_6F_3	4.9	6.6	0.4	---	7.1	2.4
C_5F_3	2.3	2.6	---	0.5	0.4	2.5
RS	---	---	1.6	5.1	---	---
RX	---	---	1.6	---	---	---
R	---	9.7	68.3	9.4	(See C_6F_5)	
PXF	(See PF_2)	(See PF_2)	(See PF_2)	(See PF_2)	(PF_2)	5.1

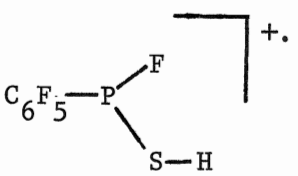
dance of the key ions shows a definite preference toward loss of a C_6F_5S radical as compared to CH_3S. For R = tC_4H_9, the abundances of C_6F_5PF and C_4H_9S are comparable suggesting a situation of low selectivity for the process presented in the diagram below. Here we speak of selectivity



in the sense of charge distribution since it is clearly apparent that there is no C_6F_5S formed by rearrangement. One can discuss the case of R = C_2H_5 by considering the ($M-C_2H_4$) peak, namely (II) as a "pseudo-parent" which loses HS to yield a rather abundant $C_6F_5PF^+$ ion. This is admittedly a naive approach since it is just as likely that the ion formed by loss of ethylene will already have hydrogen bonded to sulphur as in (III).



(II)



(III)

Evidence for halogen transfer rearrangement is again seen in the data for $(C_6F_5)_2PSCl$, where PFCl is prominent.

(c) Phosphinyl Halides (RR'POX)

The partial mass spectra of these compounds are shown in Table 8. A characteristic of all the earlier examples of such phosphinyl systems was a preponderance of ions containing the P-O linkage and such is still the case with the compounds described here. All the species studied gave strong molecular ions though the spectra do show definite influences due to the R,R' substituents.

The three examples of C_6F_5 substitution give rise to similar spectral patterns even though the intensities of individual ions vary considerably. A major factor inducing this behaviour stems from the stability which the R' substituent exerts on the system and the ability of this fragment to absorb the positive charge after P-R' cleavage. Thus, for the cases where R' is phenyl or tertiary butyl, the stability of the R' cation in each case is clearly evident from its high abundance. In contrast, where R' is methyl, the ion abundance is more evenly distributed among fragment ions.

The spectrum of $(C_6H_5)_2POF$ is somewhat different from those of the derivatives mentioned above and is reminiscent of the behaviour of triphenyl phosphine oxide. In both cases, the base peak is formed by loss of a hydrogen atom

TABLE 8

PARTIAL MASS SPECTRA OF RR'POF

Ion^+ R = R' =	C_6F_5 CH_3	C_6F_5 $t\text{-}C_4H_9$	C_6F_5 C_6H_5	C_6H_5 C_6H_5
M	13.5	5.6	7.3	11.7
M-H	1.2	0.6	0.4	26.4
$M\text{-}H_2$	9.1	0.3	---	---
M-F	1.5	---	5.5	---
M-HF	---	---	8.2	0.4
M-H-HF	---	---	---	6.1
M-O	0.3	---	---	---
M-R	3.5	---	0.9	---
M-R'	4.9	0.7	---	---
RPF	0.3	2.5	0.6	4.7
R'PF	3.7	---	3.9	(RPF)
POF	---	---	---	0.2
PF_2	3.9	2.3	2.3	---
ROH	3.7	---	---	---
RO-F	4.8	3.4	---	---
RO-2F	0.8	0.2	---	---
RR'	---	---	0.6	0.5
RR'-H	2.7	---	---	1.0
$RR'\text{-}H_2$	---	---	0.8	3.8
RR'-HF	1.7	---	2.2	---
R	1.7	2.1	0.7	9.9
R'	---	14.8	15.9	(R)

which then loses a neutral fragment to give an ion which is identical as shown in Figure 8.

The only evidence for rearrangements of the types described for the sulphide derivatives are the oxygen-fluorocarbon fragments observed for R' = CH_3 and t-C_4H_9, these being relevant to the transformation $>P(R)=O \rightleftharpoons >P-OR$ where R = C_6F_5. These are significant grounds for consideration of the second type of rearrangement, namely bond formation between substituents. In all the cases studied, fragments are observed which have resulted from whole or partial fulfillment of this transformation. The significant contributions to this sequence are as follows:

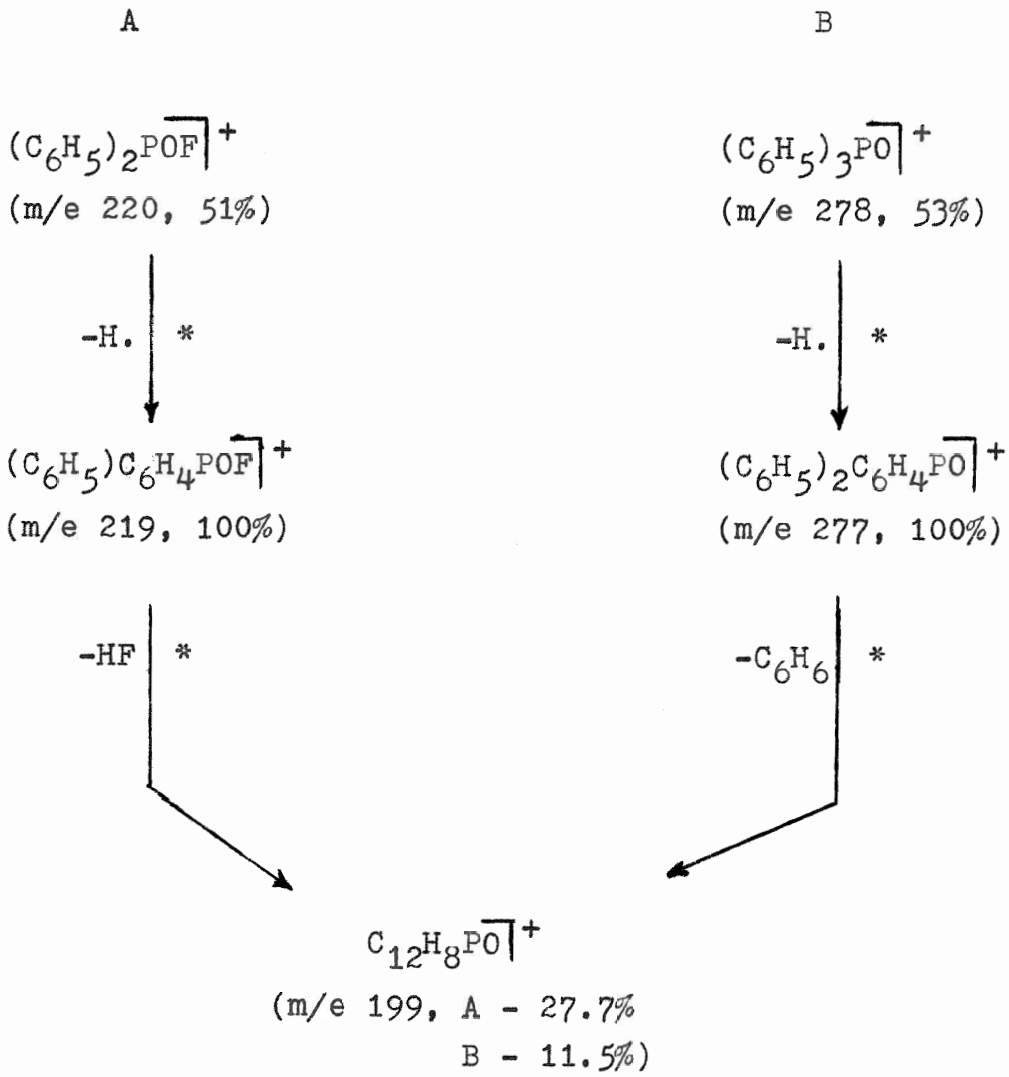
Parent Ion	Significant Coupled Fragment
$C_6F_5(CH_3)POF$ +	$C_6F_5CH_2$ +
$C_6F_5(t\text{-}C_4H_9)POF$ +	$C_6F_5CH_2$ +
$C_6F_5(C_6H_5)POF$ +	$C_{12}F_4H_4$ +
$C_6H_5(C_6H_5)POF$ +	$C_{12}H_8$ +

(d) Miscellaneous Species

(a) Tris (pentafluorophenyl) Phosphorous Difluoride

The partial mass spectrum of this compound is shown in Table 9. In contrast to the phosphoranes $(C_6F_5)_3PCl_2$ and $(C_6F_5)_2PCl_3$ which were shown by Miller[13] to give no molecular ions, decomposing by loss of a halogen molecule, the difluoride studied here gives a reasonably abundant

FIGUE 8


A
B
$(C_6H_5)_2POF^+$
(m/e 220, 51%)
$(C_6H_5)_3PO^+$
(m/e 278, 53%)
-H. *
-H. *
$(C_6H_5)C_6H_4POF^+$
(m/e 219, 100%)
$(C_6H_5)_2C_6H_4PO^+$
(m/e 277, 100%)
-HF *
$-C_6H_6$ *
$C_{12}H_8PO^+$
(m/e 199, A - 27.7%
B - 11.5%)

molecular ion (ca 4% relative abundance) and decomposes by a somewhat different route. The preferred breakdown pathway involves loss of C_6F_5 followed by loss of either fluorine, PF_2 and CF_3, C_6F_6 or C_6F_4. All of these processes are supported by metastable ions.

In addition to the major fragments described above, a variety of fluoroaromatic ions are observed which carry a significant amount of the ion current (see Table 9). These ions have been shown to be common entities in studies of other Group V compounds[14] and various miscellaneous systems[8,10]. The significant abundance of PF_2, PF_3 and PF_4 species confirms the operation of halogen transfer processes and provides evidence for the pathways giving rise to large fluoroaromatic fragments.

(b) Ethyl bis(pentafluorophenyl)phosphinothioite difluoride.

The partial mass spectrum of this compound is also shown in Table 9. No parent ion is observed for this compound which appears to lose a C_2H_5S radical rapidly, giving a base peak identical to that of (a). The fate of this ion is similar; the major route for decomposition apparently being through loss of hexafluorobenzene. No fragments were detected which would suggest that the previously mentioned rearrangements are reversible, i.e.

"Text continues on Page 70."

TABLE 9

MISCELLANEOUS SPECIES: PARTIAL MASS SPECTRA

$(C_6F_5)_2PF_2(SC_2H_5)$		$(C_6F_5)_3PF_2$	
Ion$^+$	Rel.Abundance	Ion$^+$	Rel.Abundance
M	0.0	M	3.6
M-F	0.3	M-F	4.3
$M-C_2H_5$	0.3	$M-F_2$	0.3
M-2F	2.9	$M-PF_3$	0.1
$M-SC_2H_5$	100.0	$(C_6F_5)_2PF_2$	100.0
$(C_6F_5)_2PS$	5.9	$(C_6F_5)_2PF$	3.1
$(C_6F_5)_2PF$	2.1	$(C_6F_5)_2P$	1.7
$(C_6F_5)_2P$	4.3	$C_6F_5PF_3$	5.6
$C_6F_5PF_3$	11.0	$C_6F_5PF_2$	2.3
$C_6F_5PF_2$	4.3	C_6F_5PF	5.5
C_6F_5PF	76.4	PF_4	2.1
C_6F_5S	3.0	PF_3	1.3
C_6F_4S	1.8	PF_2	21.0
C_6F_5	10.5	$C_{18}F_{13}$	0.2
C_6F_4	7.9	$C_{18}F_{12}$	0.2
C_6F_3	19.6	$C_{12}F_{10}$	1.6
C_5F_3	18.5	$C_{12}F_8$	2.2
PF_4	4.8	C_6F_5	5.4
PF_2	41.7	C_6F_4	5.3
PS	6.4	C_6F_3	5.9
		C_5F_3	8.0
		C_5F_2	2.1

Figure 9
The Mass Spectrum
of $(C_6H_5)P(S)F_2$
at 70 eV

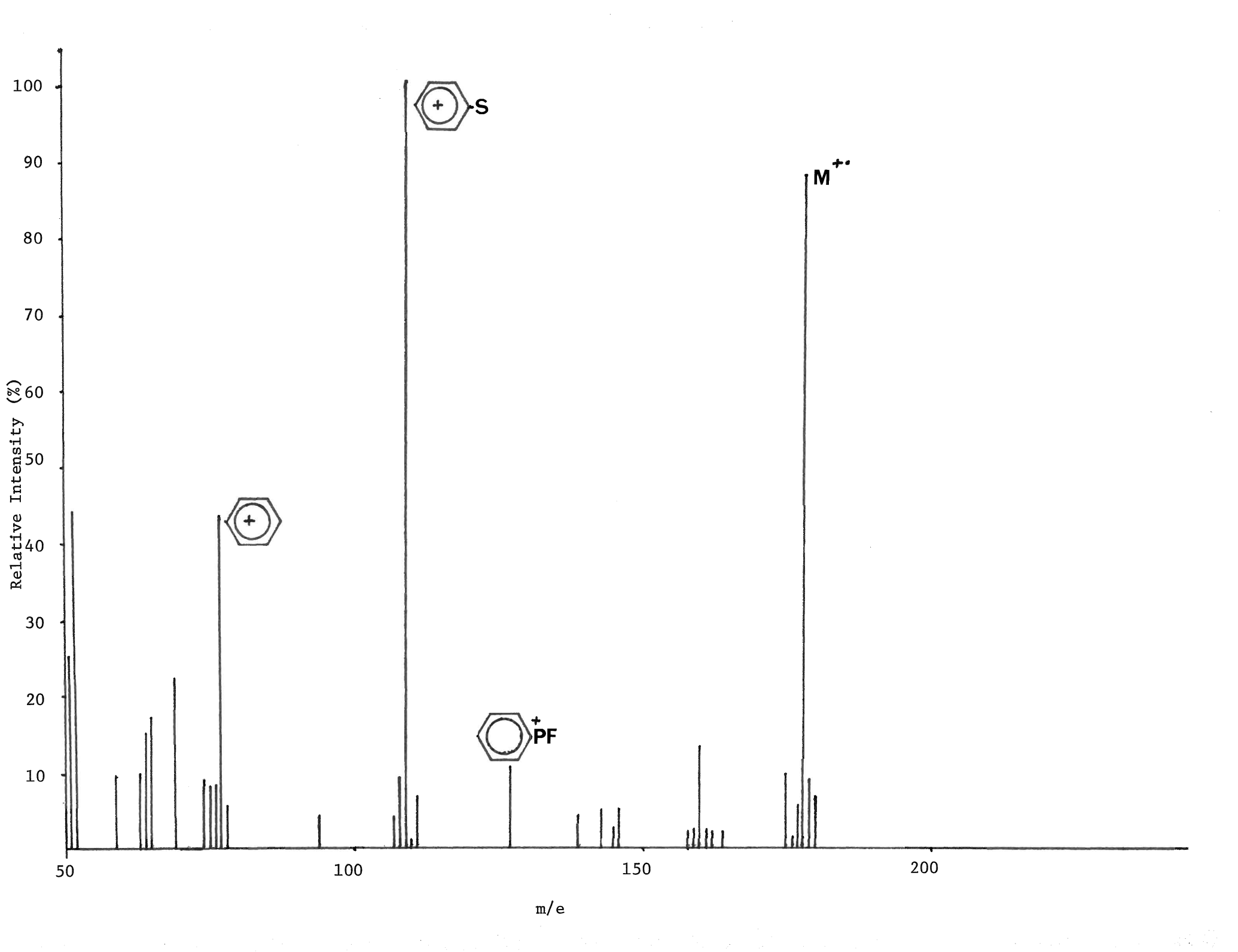

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
S
M+·
PF+
50
100
150
200
m/e

Figure 10
The Mass Spectrum
of $(C_6H_5)P(S)Cl_2$
at 70 eV

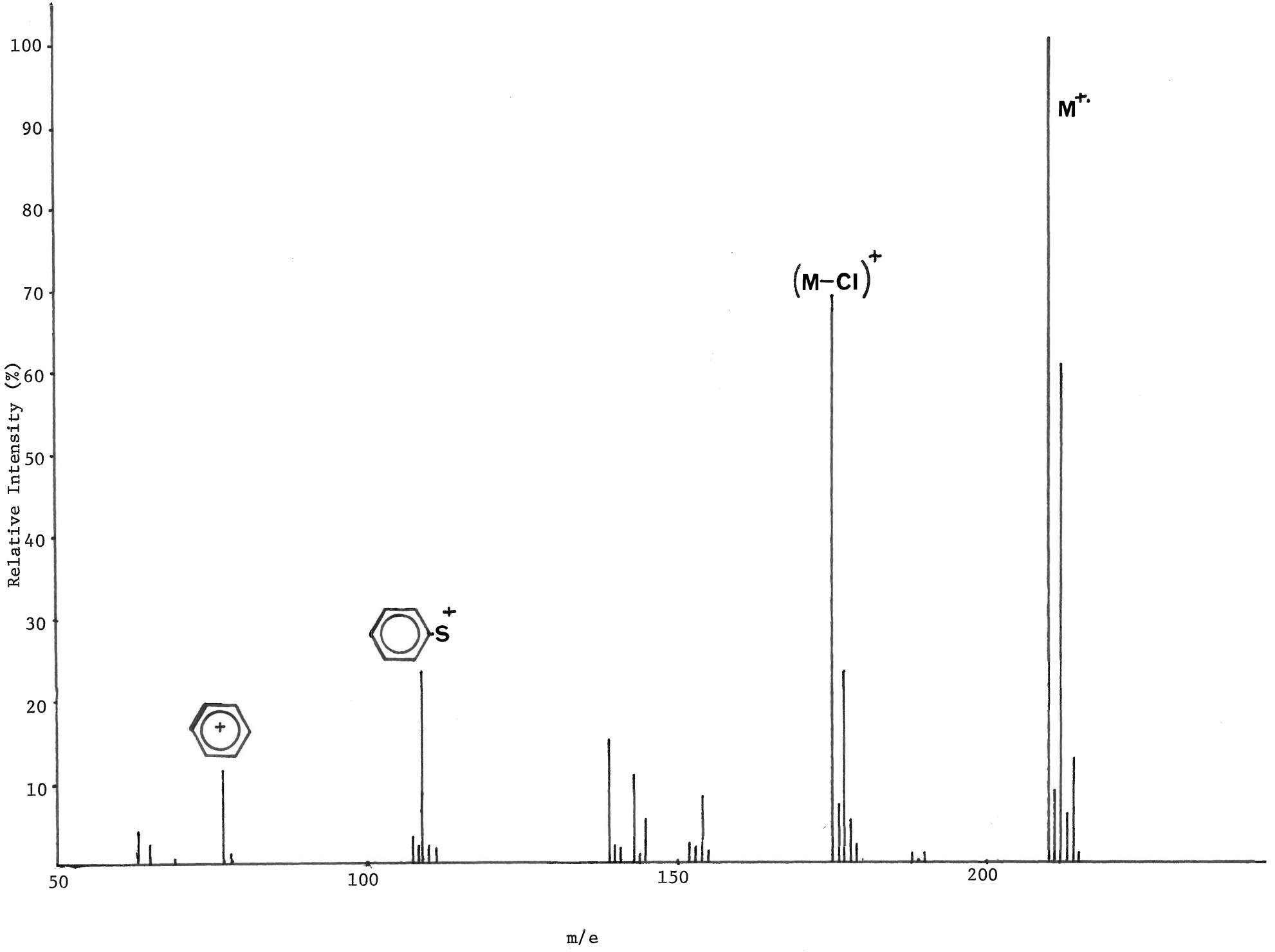

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
m/e
M+·
(M–Cl)+
S+

Figure 11
The Mass Spectrum
of $(C_6F_5)P(S)F_2$
at 70 eV

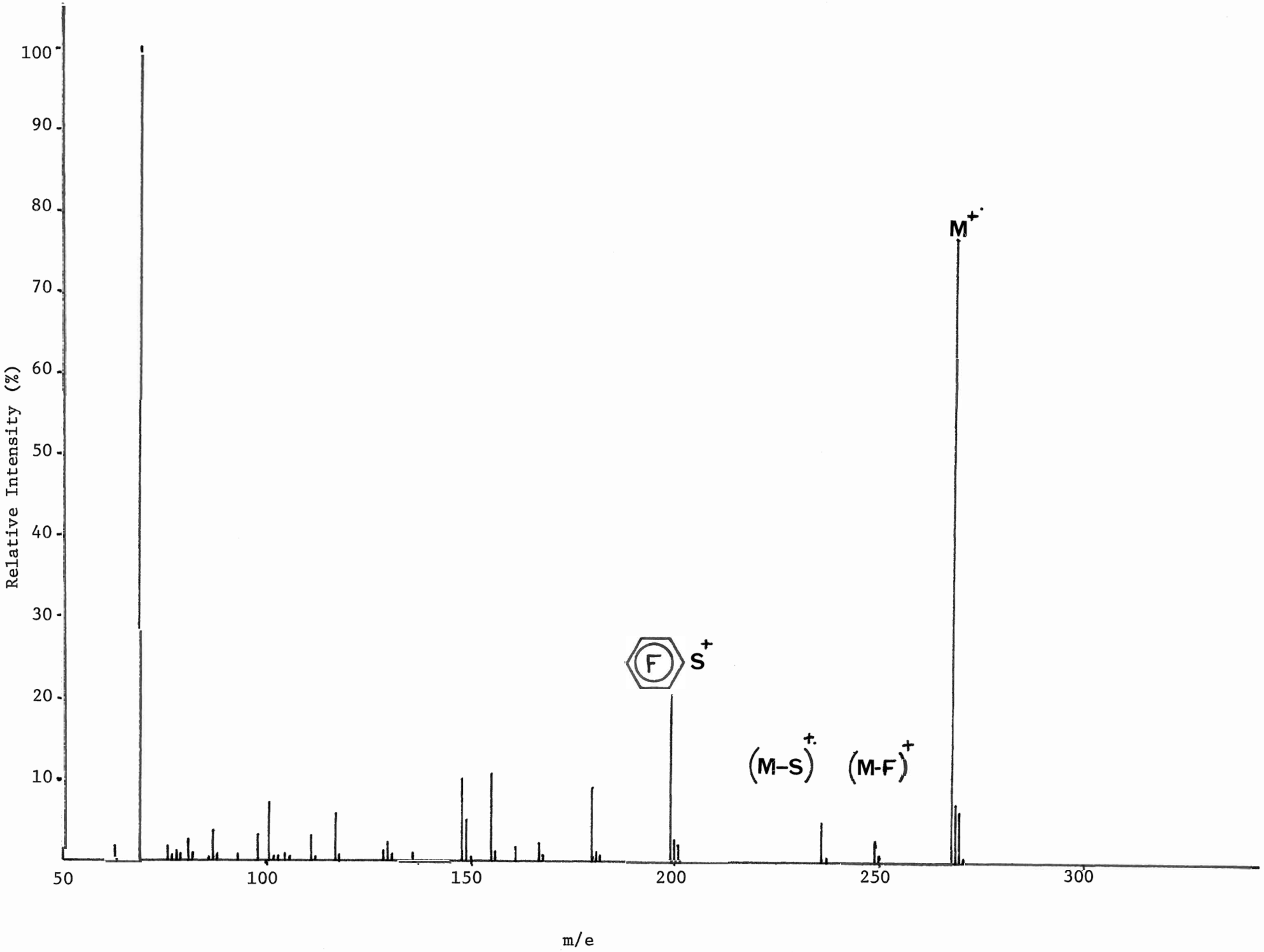

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
m/e
M+·
F S+
(M–S)+·
(M-F)+

Figure 12
The Mass Spectrum
of $(C_6F_5)P(S)Cl_2$
at 70 eV

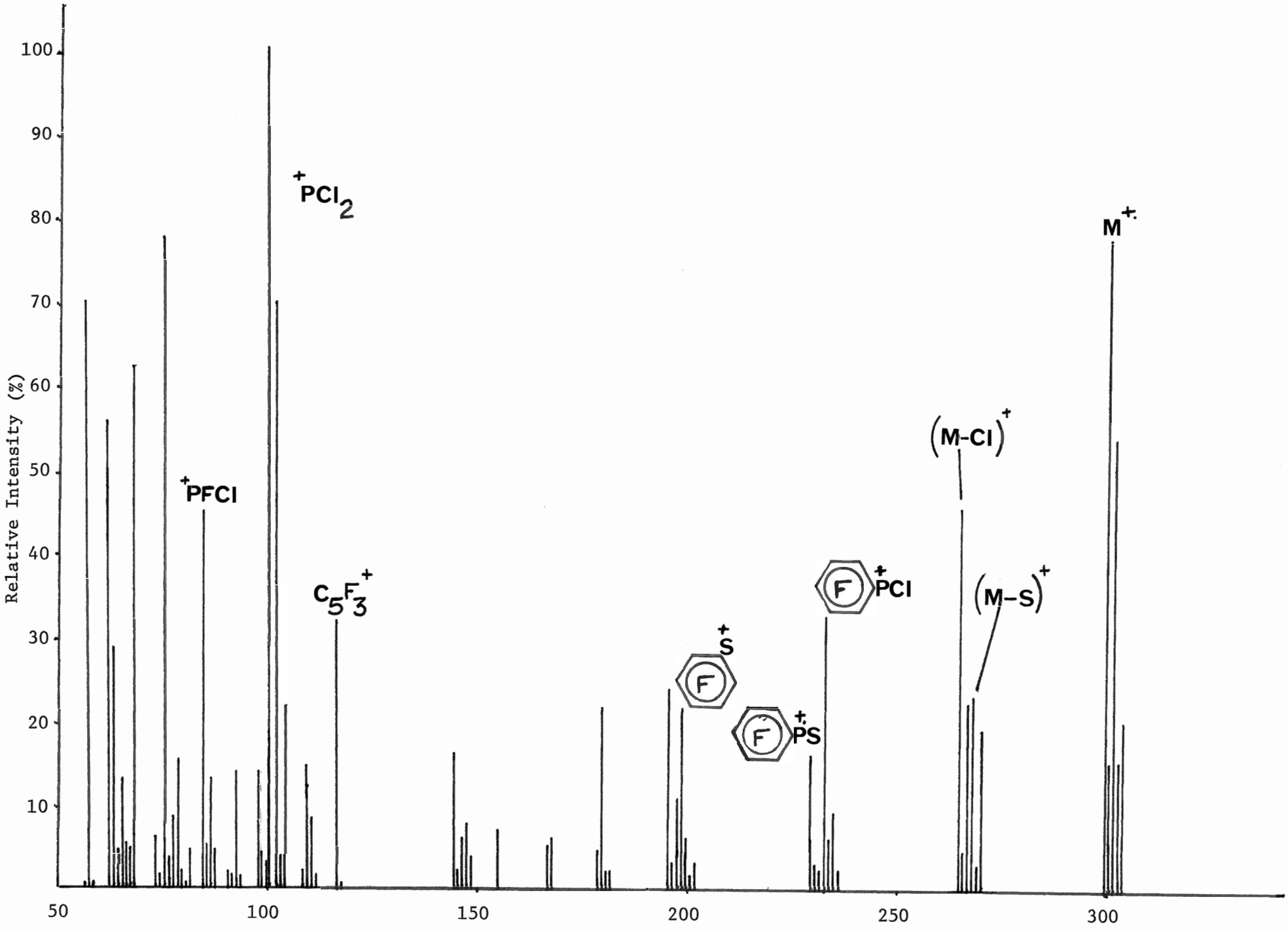

Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
+PCl2
+PFCl
C5F3+
+S
F
F
+PS
F
+PCl
(M-Cl)+
(M-S)+
M+.

Figure 13
The Mass Spectrum
of $(C_6F_5)P(S)Br_2$
at 70 eV

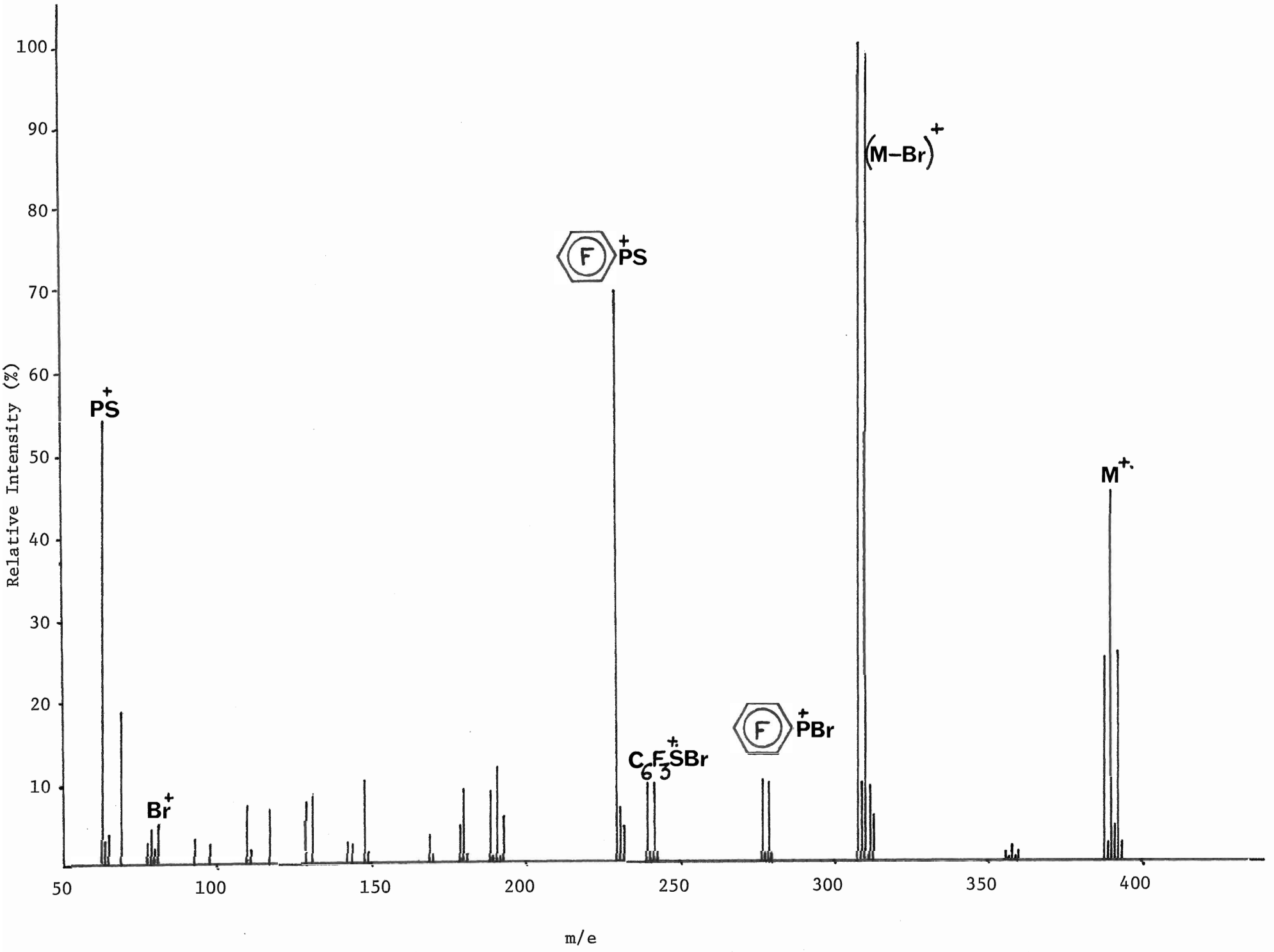
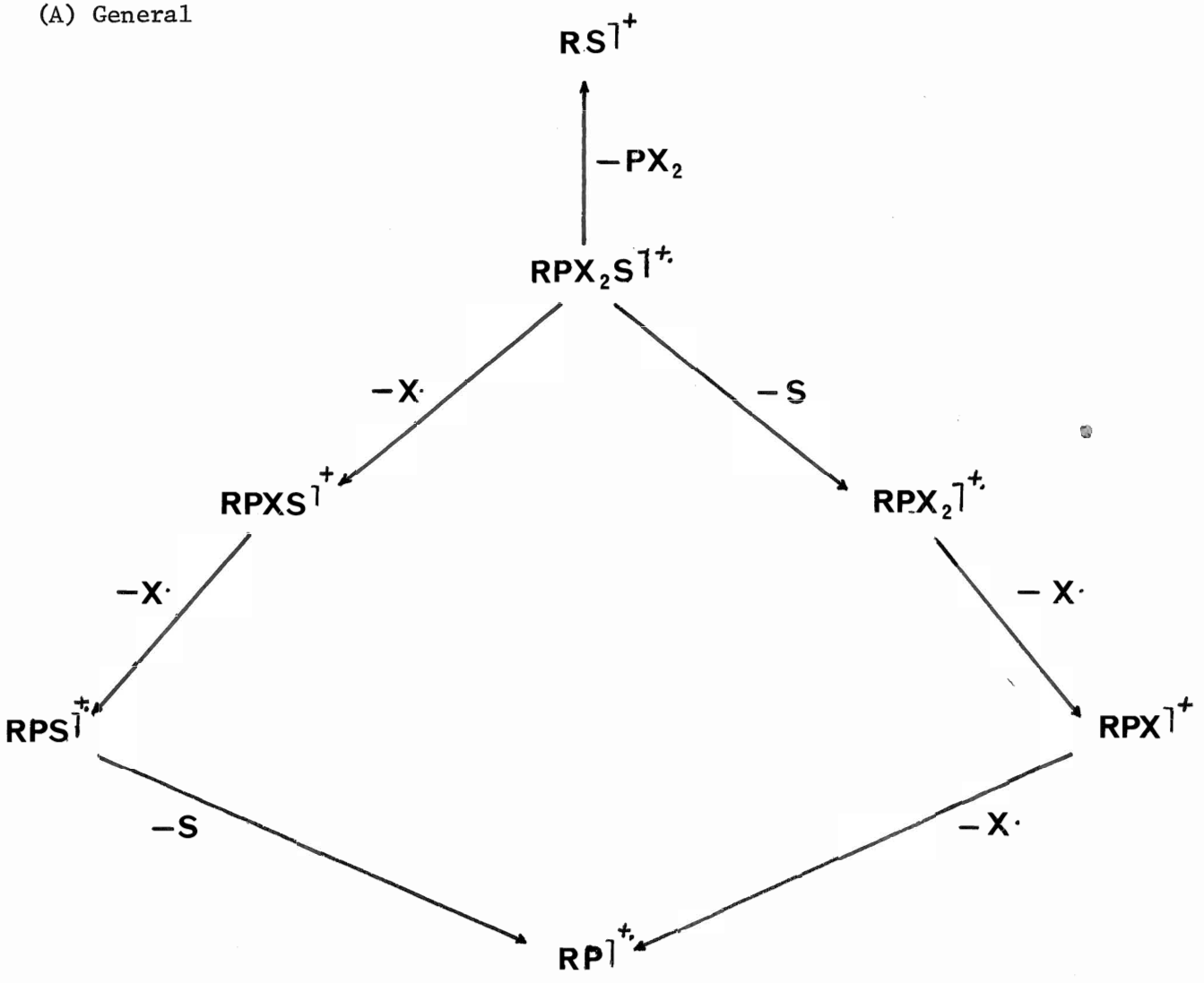

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
PS+
Br+
F PS+
C6F3S+Br
F PBr+
(M–Br)+
M+·
50
100
150
200
250
300
350
400
m/e

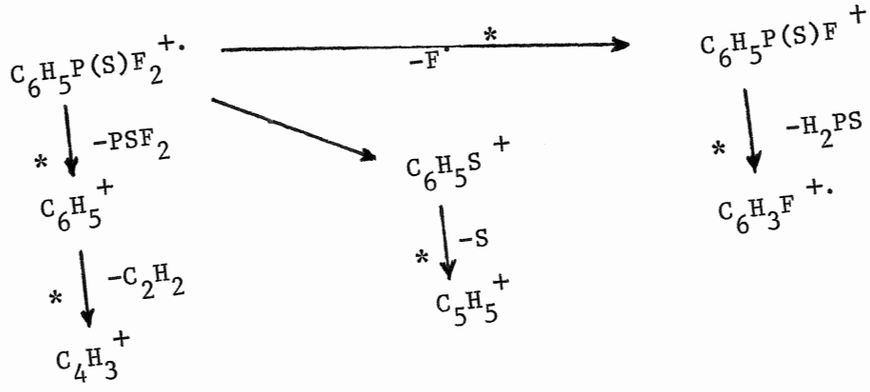
Figure 14
Fragmentation Schemes
for the series $RP(S)X_2$

(A) General
(B) X = F, R= C_6H_5
(C) X = Cl, R = C_6H_5
(D) X = F, R = C_6F_5
(E) X = Cl, R = C_6F_5
(F) X = Br, R = C_6F_5

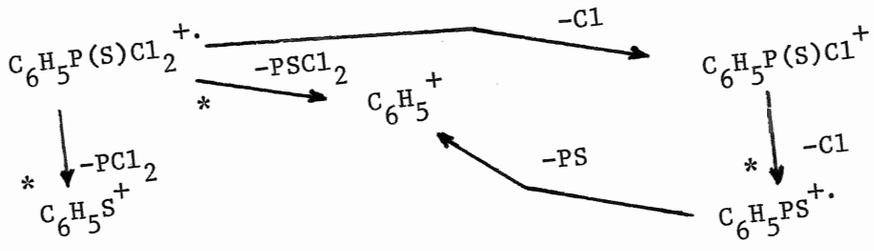
(A) General



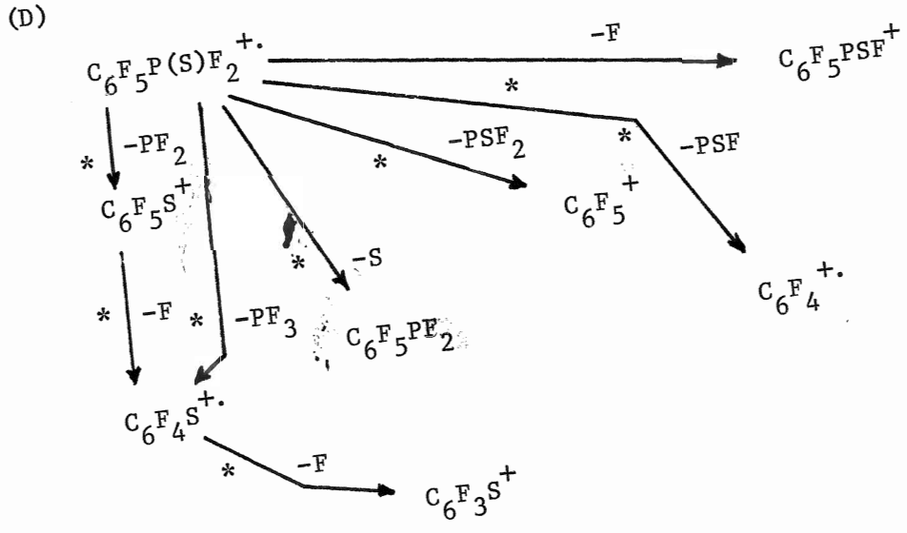
(B)


$C_6H_5P(S)F_2^{+\cdot}$
$-F^{\cdot}$
$C_6H_5P(S)F^+$
$-PSF_2$
$-H_2PS$
$C_6H_5^+$
$C_6H_5S^+$
$C_6H_3F^{+\cdot}$
$-C_2H_2$
$-S$
$C_4H_3^+$
$C_5H_5^+$

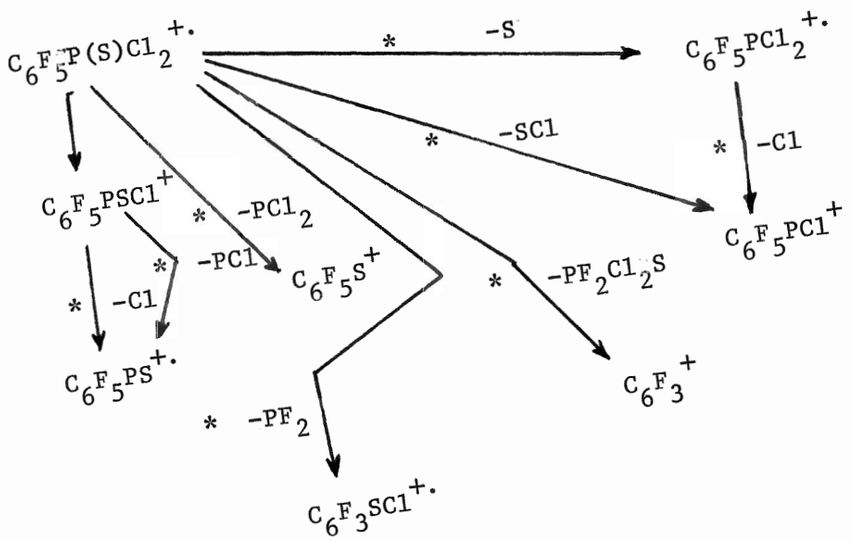
(C)


$C_6H_5P(S)Cl_2^{+\cdot}$
$-Cl$
$C_6H_5P(S)Cl^+$
$-PSCl_2$
$C_6H_5^+$
$-PCl_2$
$-PS$
$-Cl$
$C_6H_5S^+$
$C_6H_5PS^{+\cdot}$

(D)


$C_6F_5P(S)F_2^{+\cdot}$
$-F$
$C_6F_5PSF^+$
$-PF_2$
$-PSF_2$
$-PSF$
$C_6F_5S^+$
$C_6F_5^+$
$-S$
$C_6F_4^{+\cdot}$
$-F$
$-PF_3$
$C_6F_5PF_2$
$C_6F_4S^{+\cdot}$
$-F$
$C_6F_3S^+$

(E)


$C_6F_5P(S)Cl_2^{+\cdot}$
*
-S
$C_6F_5PCl_2^{+\cdot}$
*
-SCl
*
-Cl
$C_6F_5PCl^+$
$C_6F_5PSCl^+$
*
$-PCl_2$
*
-PCl
*
-Cl
$C_6F_5S^+$
*
$-PF_2Cl_2S$
$C_6F_5PS^{+\cdot}$
$C_6F_3^+$
*
$-PF_2$
$C_6F_3SCl^{+\cdot}$

(F)

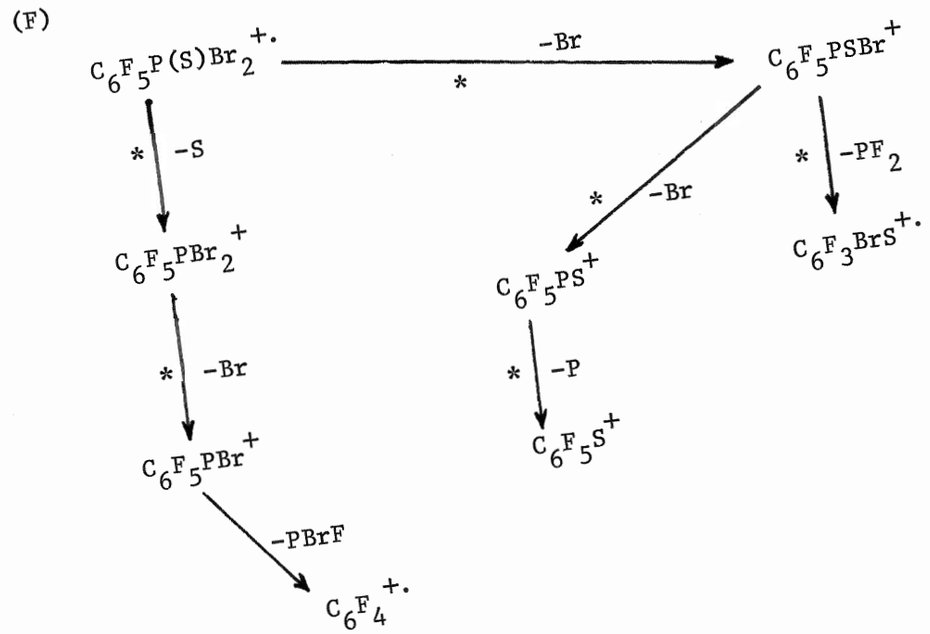

$C_6F_5P(S)Br_2^{+\cdot}$
*
-Br
$C_6F_5PSBr^+$
*
-S
*
-Br
*
$-PF_2$
$C_6F_5PBr_2^+$
$C_6F_5PS^+$
$C_6F_3BrS^{+\cdot}$
*
-Br
*
-P
$C_6F_5PBr^+$
$C_6F_5S^+$
-PBrF
$C_6F_4^{+\cdot}$

Figure 15
The Mass Spectrum
of $(C_6F_5)(CH_3)P(S)F$
at 70 eV

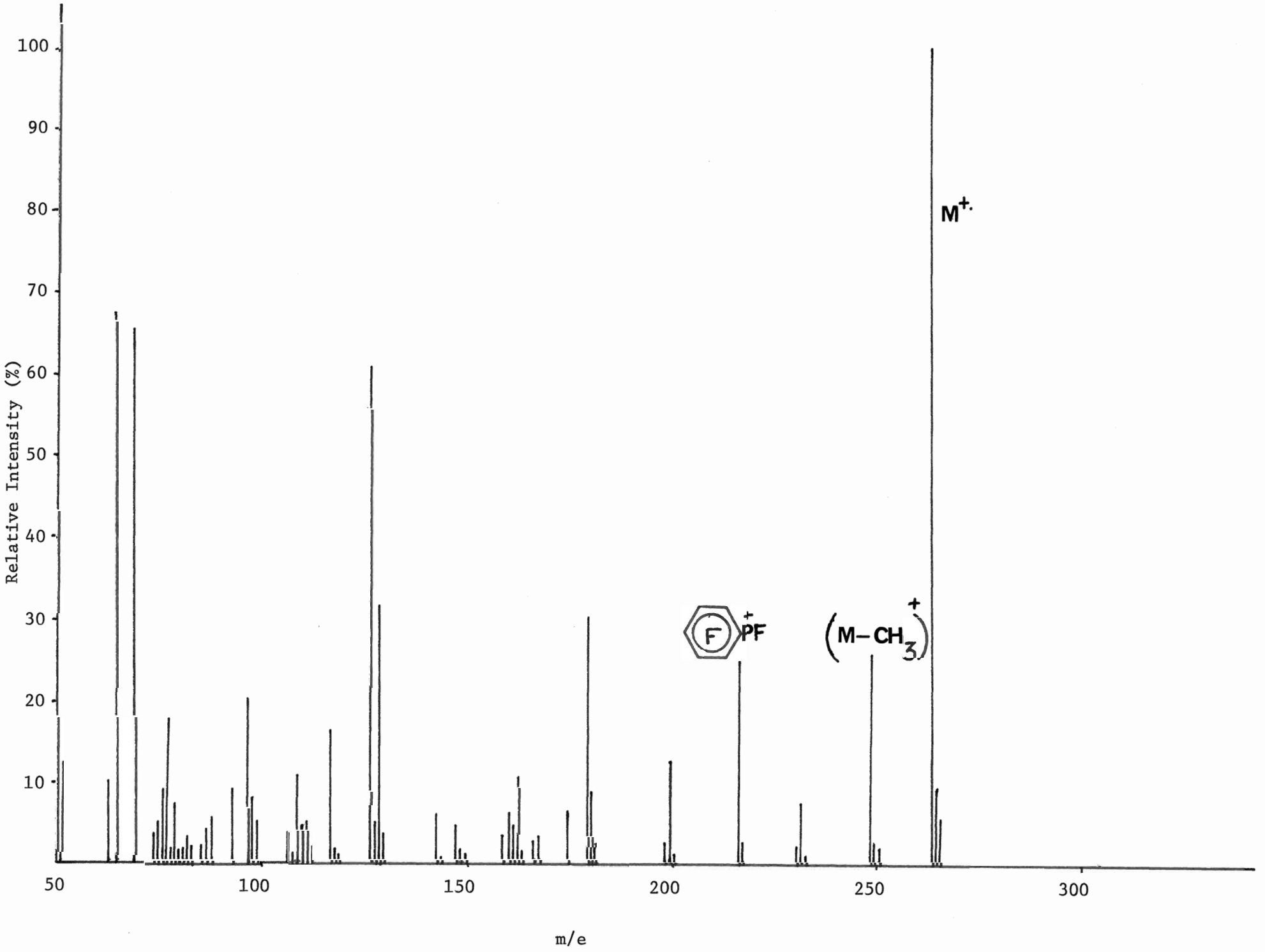

Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
m/e
M+.
F
PF+
(M−CH3)+

Figure 16
The Mass Spectrum
of $(C_6F_5)(C_2H_5)P(S)F$
at 70 eV

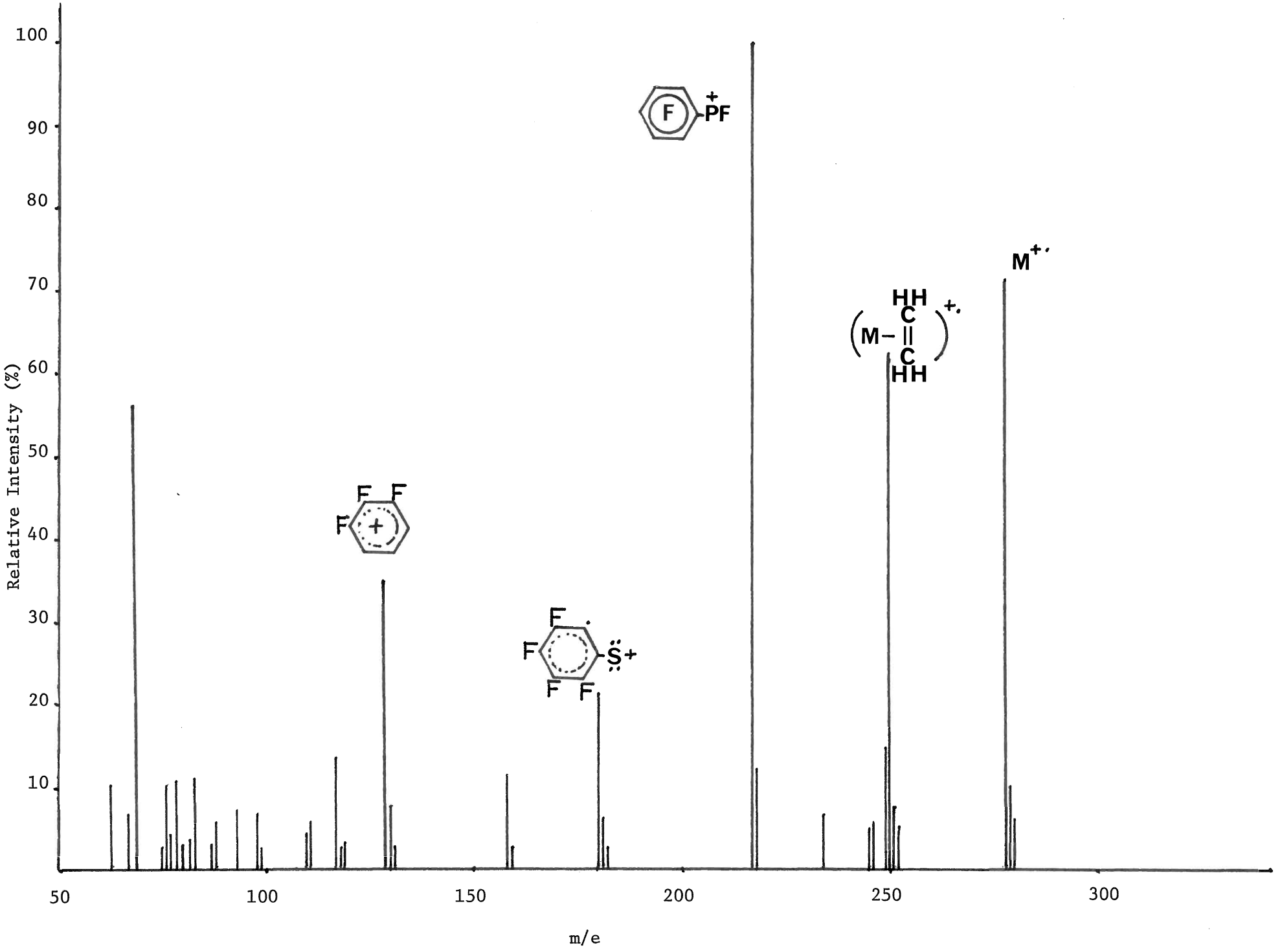

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
m/e
F
+
PF
M+·
HH
C
(M− ‖)+·
C
HH
F F
F
+
F
F
F
S+
F F

Figure 17
The Mass Spectrum
of $(C_6F_5)(t\text{-}C_4H_9)P(S)F$
at 70 eV

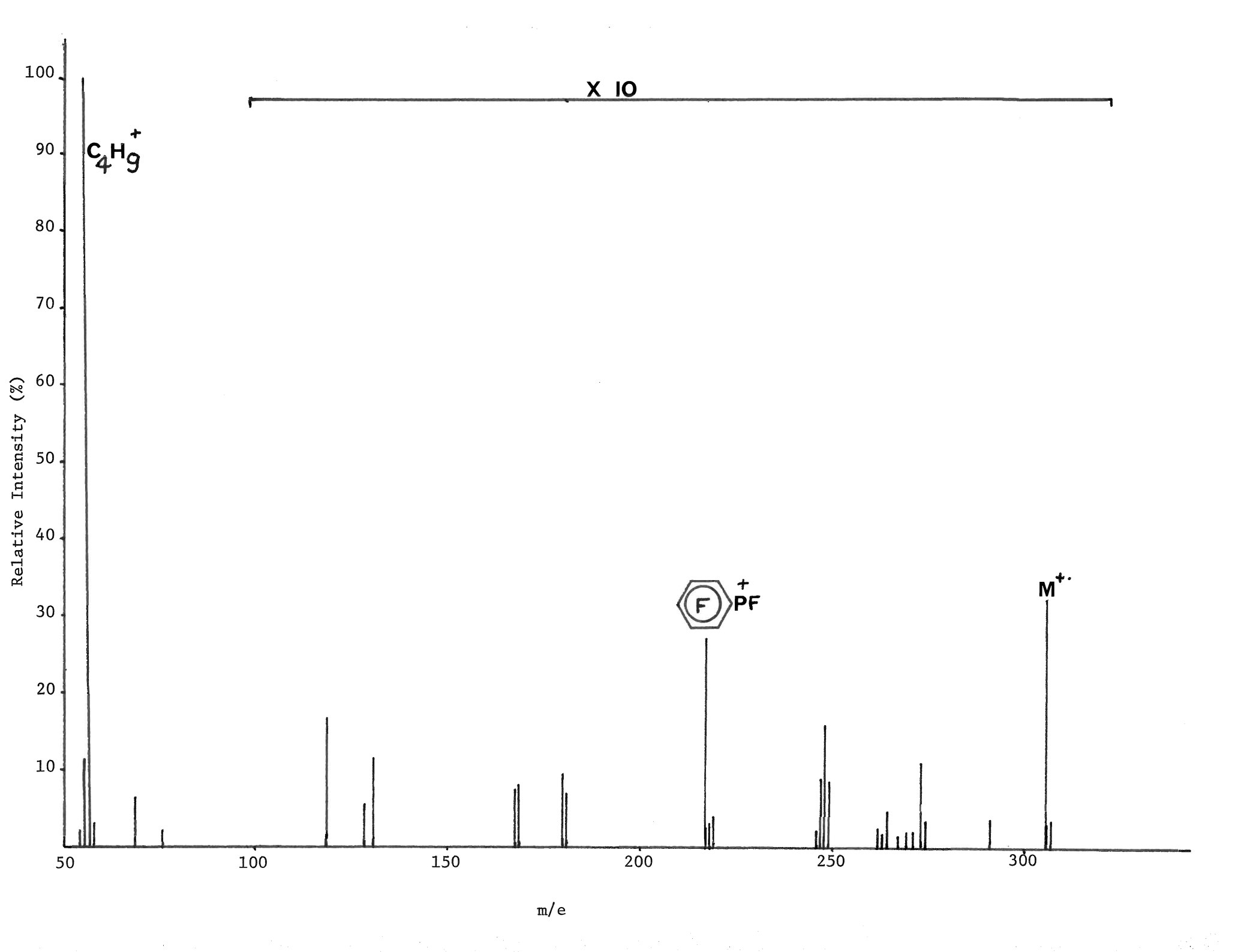

X 10
$C_4H_9^+$
F
PF
$M^{+\cdot}$
Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
m/e

Figure 18
The Mass Spectrum
of $(C_6F_5)(C_6H_5)P(S)F$
at 70 eV

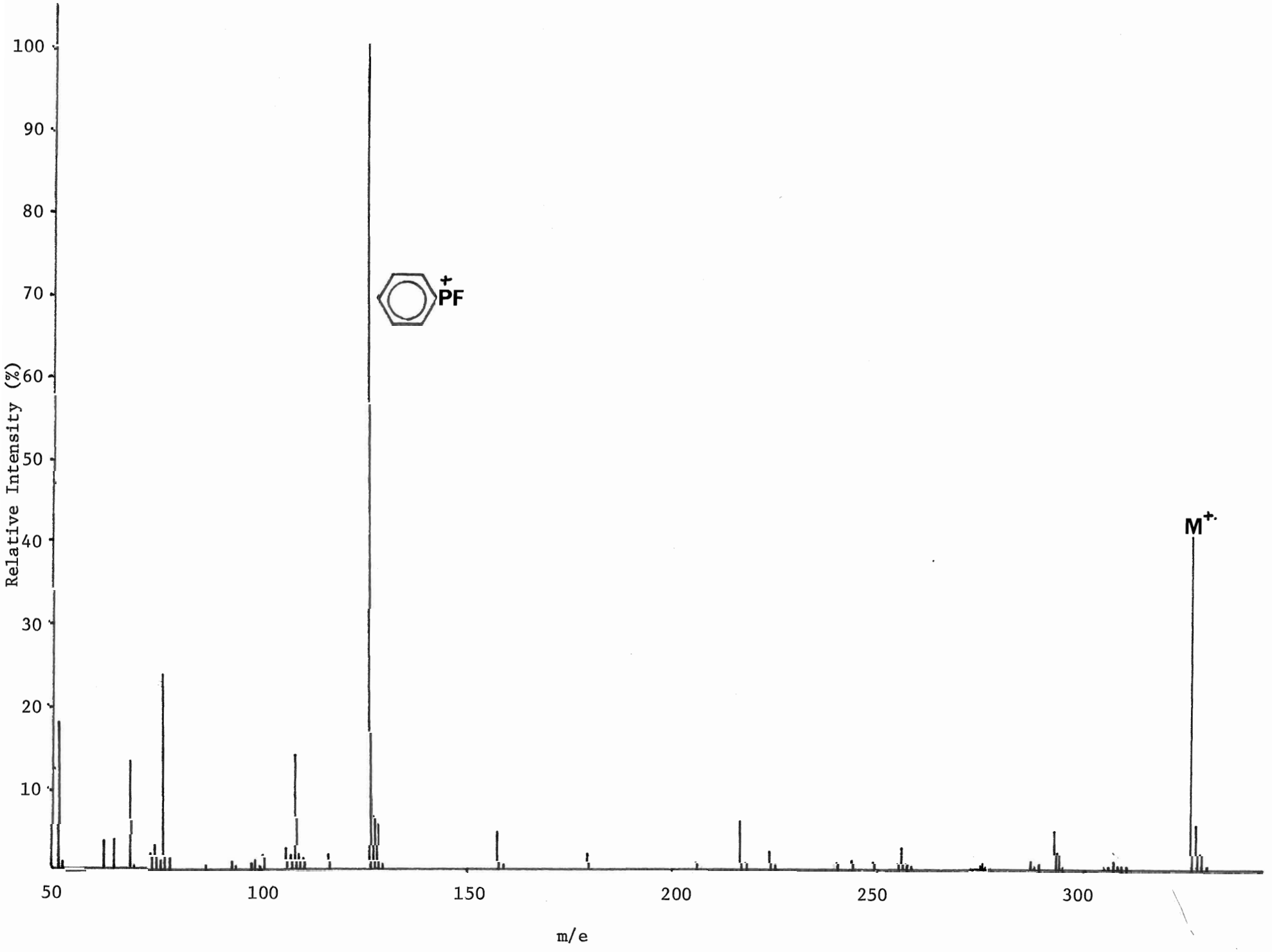

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
+
PF
M+.
50
100
150
200
250
300
m/e

Figure 19
The Mass Spectrum
of $(C_6F_5)_2P(S)F$
at 70 eV

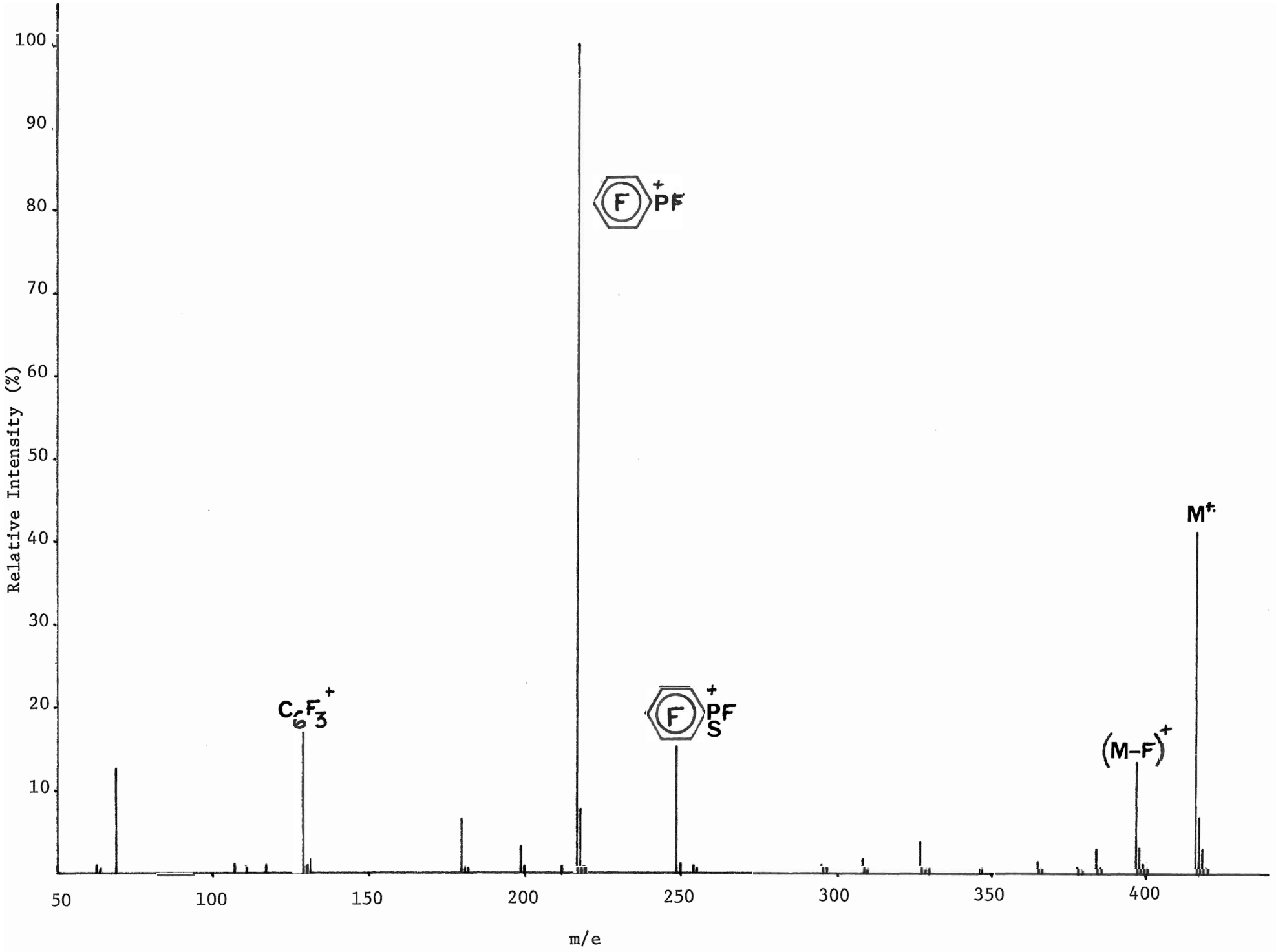

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
m/e
$C_6F_3^+$
$M^{+\cdot}$
$(M-F)^+$

Figure 20
The Mass Spectrum
of $(C_6F_5)_2P(S)Cl$
at 70 eV

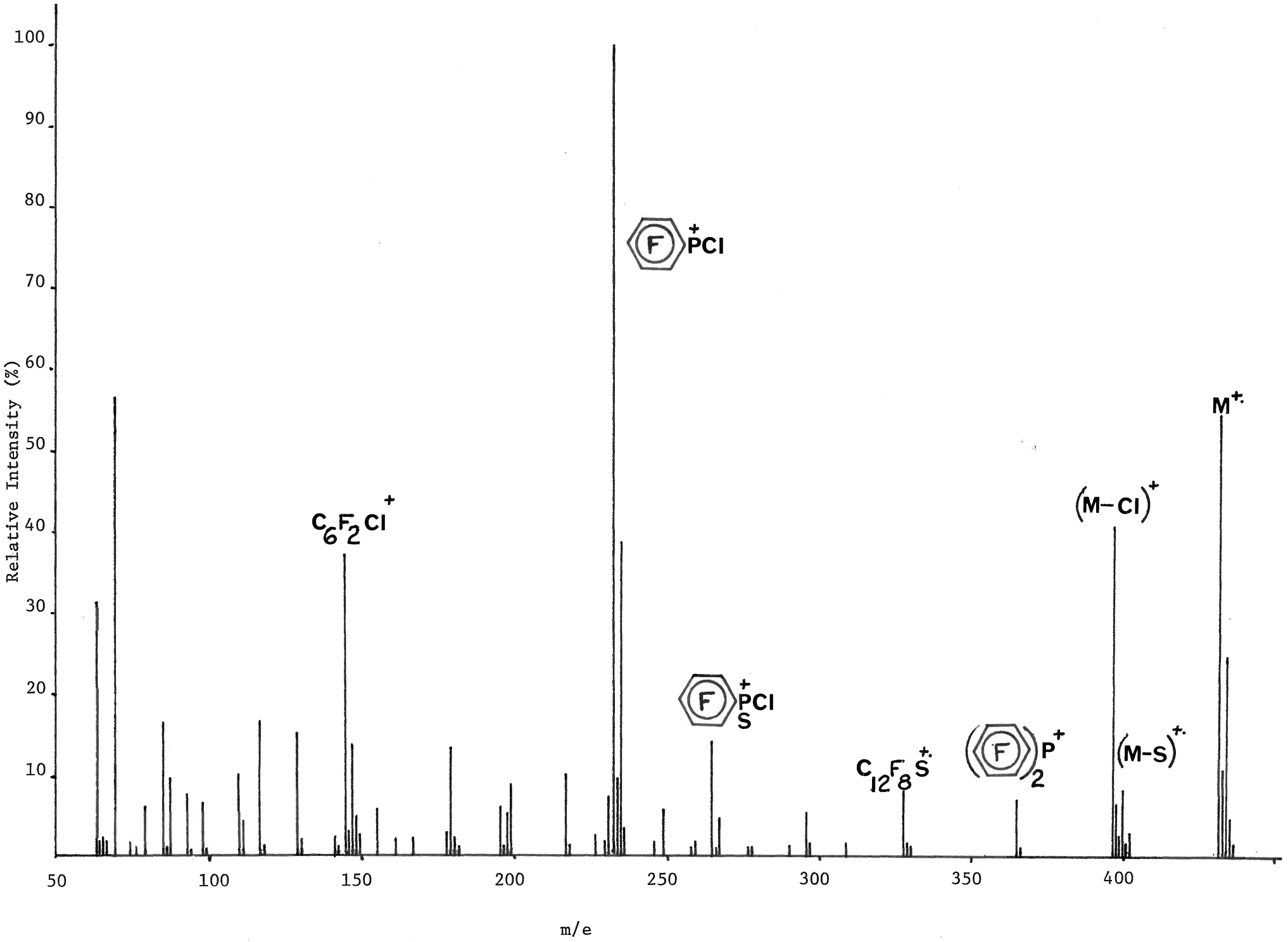

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
m/e
C6F2Cl+
F PCl+
F PCl+
S
C12F8S+·
F 2P+
(M−Cl)+
(M-S)+·
M+·

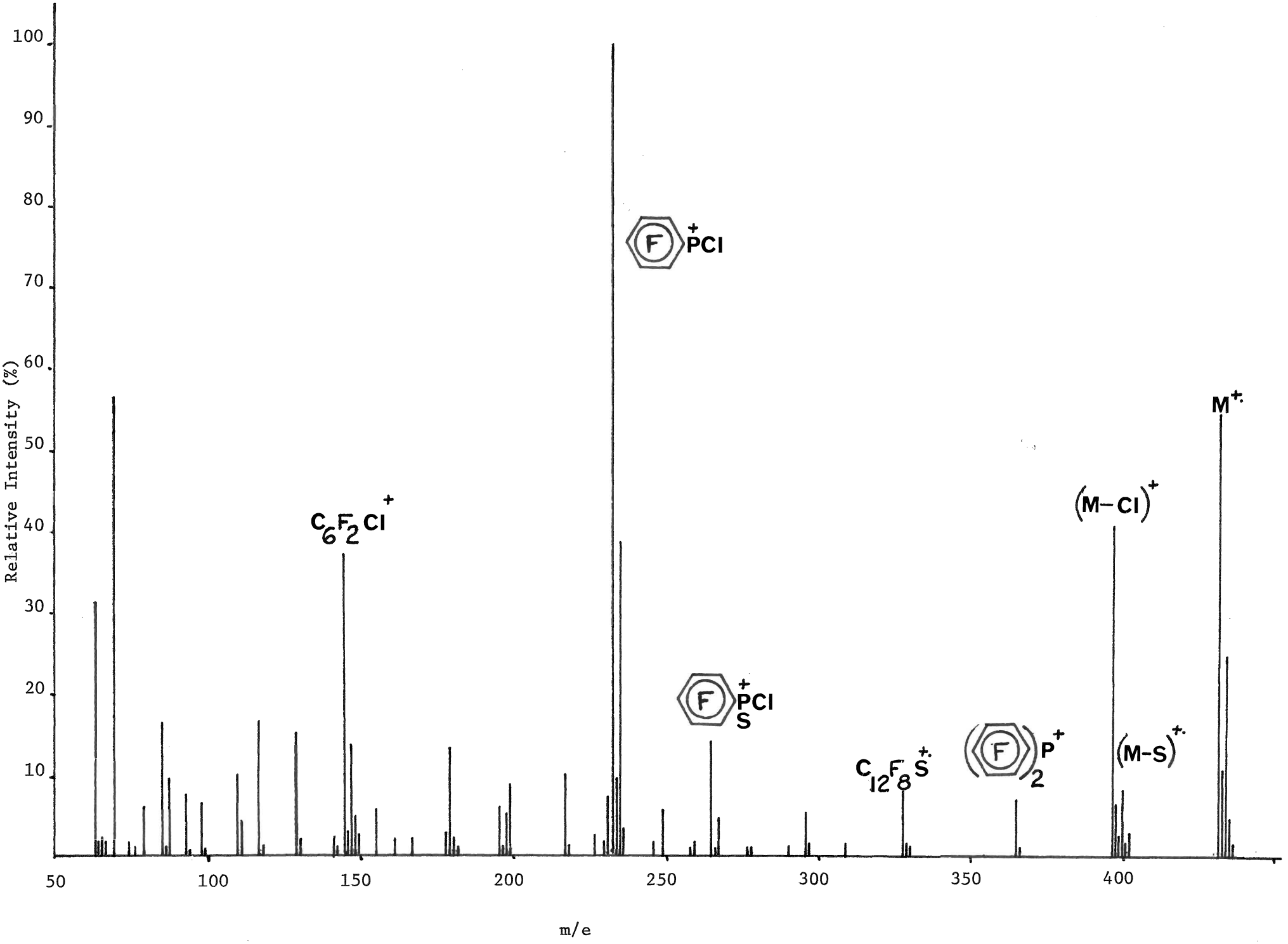
Figure 21
Fragmentation Schemes
for the series $(C_6F_5)RP(S)X$

(A) General
(B) R = CH_3, X = F
(C) R = C_2H_5, "
(D) R = t-C_4H_9, "
(E) R = C_6H_5, "
(F) R = C_6F_5, "
(G) R = C_6F_5, X = Cl

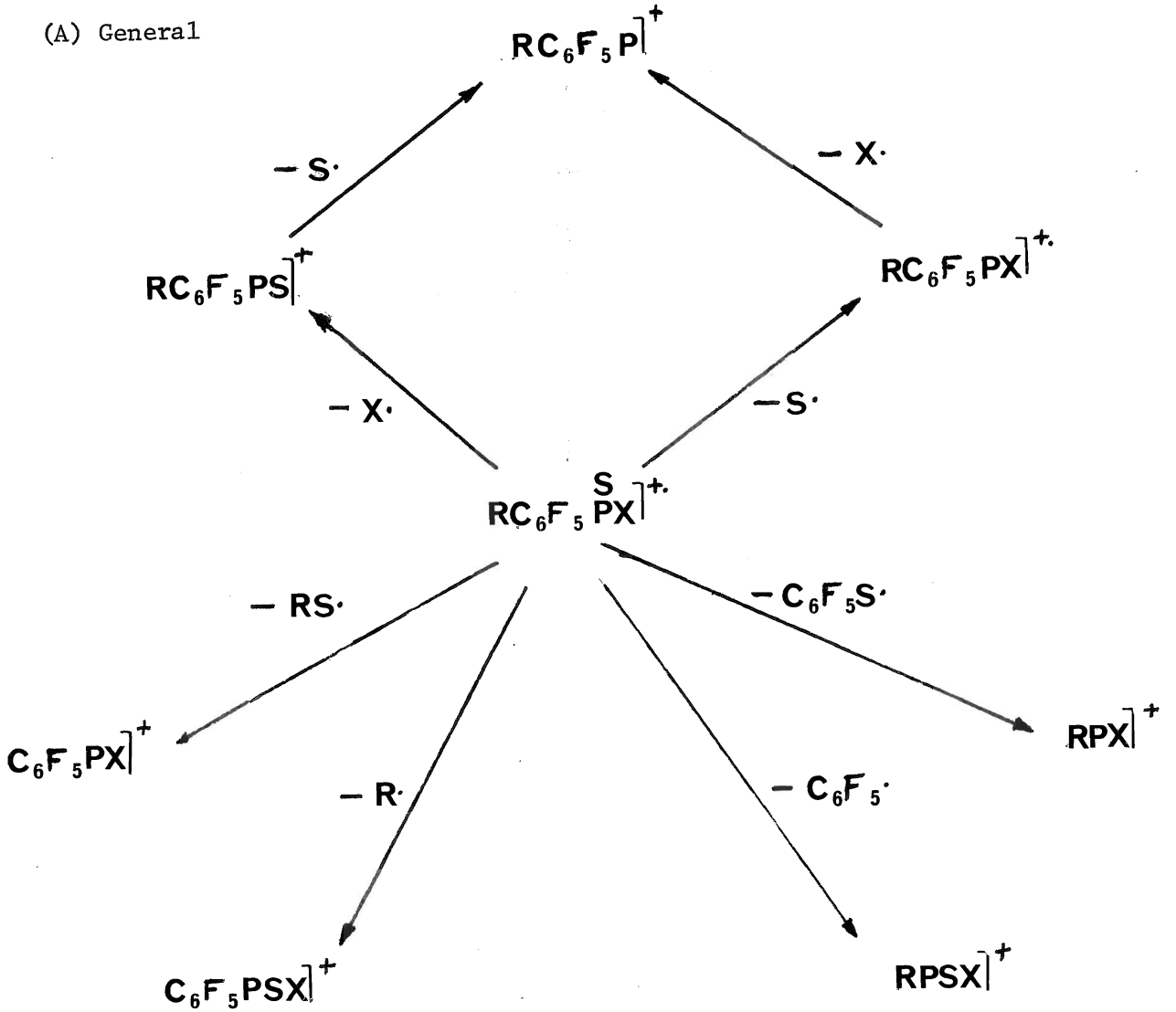
Figure 20
The Mass Spectrum
of $(C_6F_5)_2P(S)Cl$
at 70 eV

Figure 21
Fragmentation Schemes
for the series $(C_6F_5)RP(S)X$

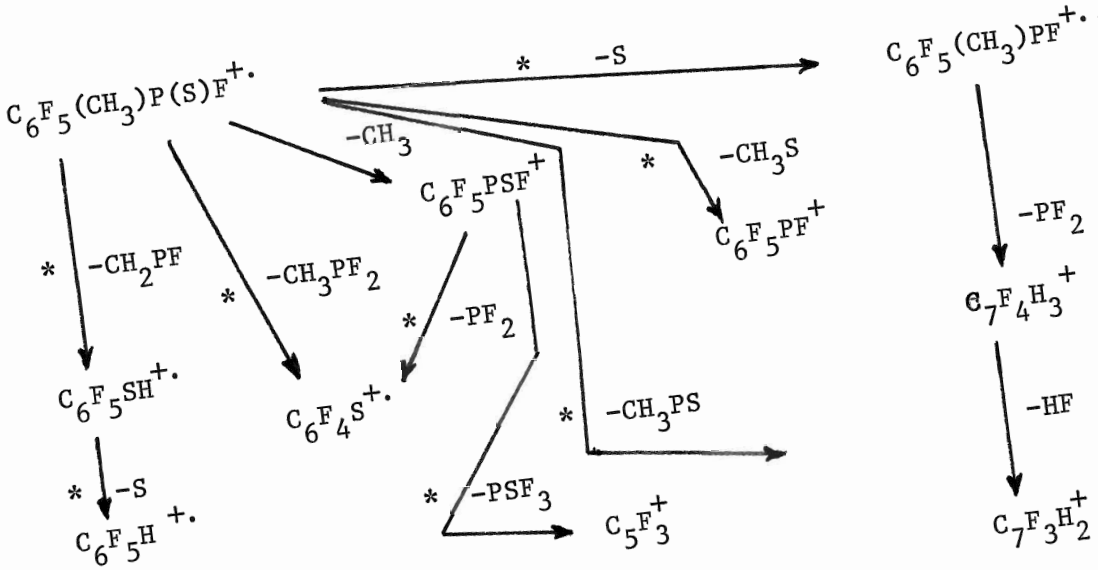
(A) General
(B) R = CH_3, X = F
(C) R = C_2H_5, "
(D) R = t-C_4H_9, "
(E) R = C_6H_5, "
(F) R = C_6F_5, "
(G) R = C_6F_5, X = Cl


100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
m/e
$C_6F_2Cl^+$
$C_{12}F_8S^{+\cdot}$
$(M-Cl)^+$
$(M-S)^{+\cdot}$
$M^{+\cdot}$

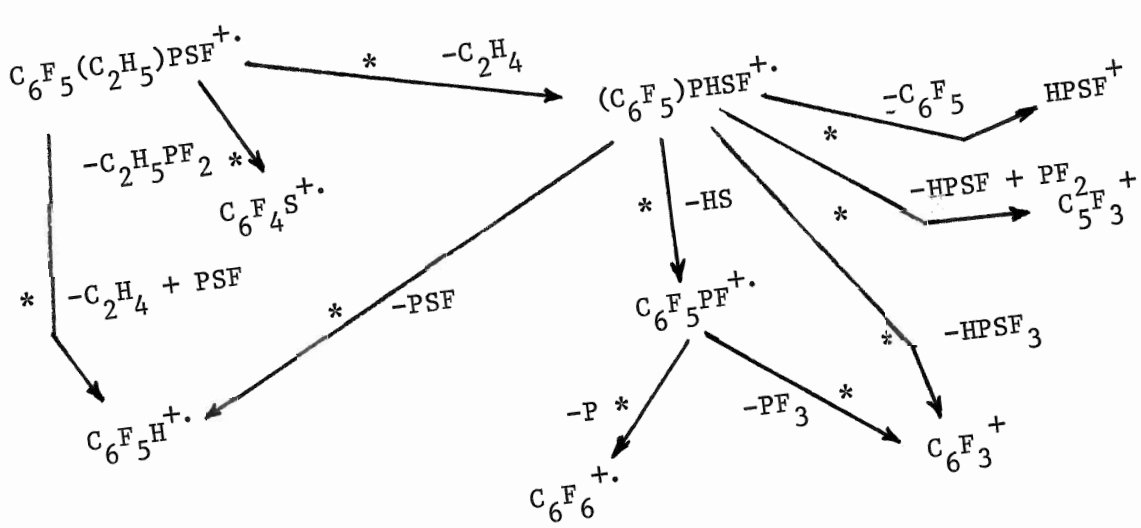
(A) General


$RC_6F_5P]^+$
$RC_6F_5PS]^+$
$RC_6F_5PX]^{+\cdot}$
$RC_6F_5\overset{S}{P}X]^{+\cdot}$
$C_6F_5PX]^+$
$C_6F_5PSX]^+$
$RPX]^+$
$RPSX]^+$
$-S\cdot$
$-X\cdot$
$-X\cdot$
$-S\cdot$
$-RS\cdot$
$-R\cdot$
$-C_6F_5S\cdot$
$-C_6F_5\cdot$

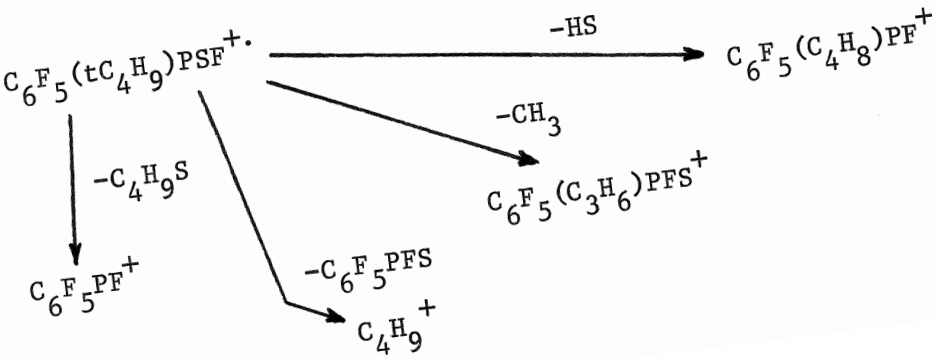
(B)


$C_6F_5(CH_3)P(S)F^{+\cdot}$
* -S
$C_6F_5(CH_3)PF^{+\cdot}$
-CH_3
$C_6F_5PSF^+$
* -CH_3S
$C_6F_5PF^+$
* -CH_2PF
* -CH_3PF_2
* -PF_2
-PF_2
$C_7F_4H_3^+$
$C_6F_5SH^{+\cdot}$
$C_6F_4S^{+\cdot}$
* -CH_3PS
-HF
* -S
$C_6F_5H^{+\cdot}$
* -PSF_3
$C_5F_3^+$
$C_7F_3H_2^+$

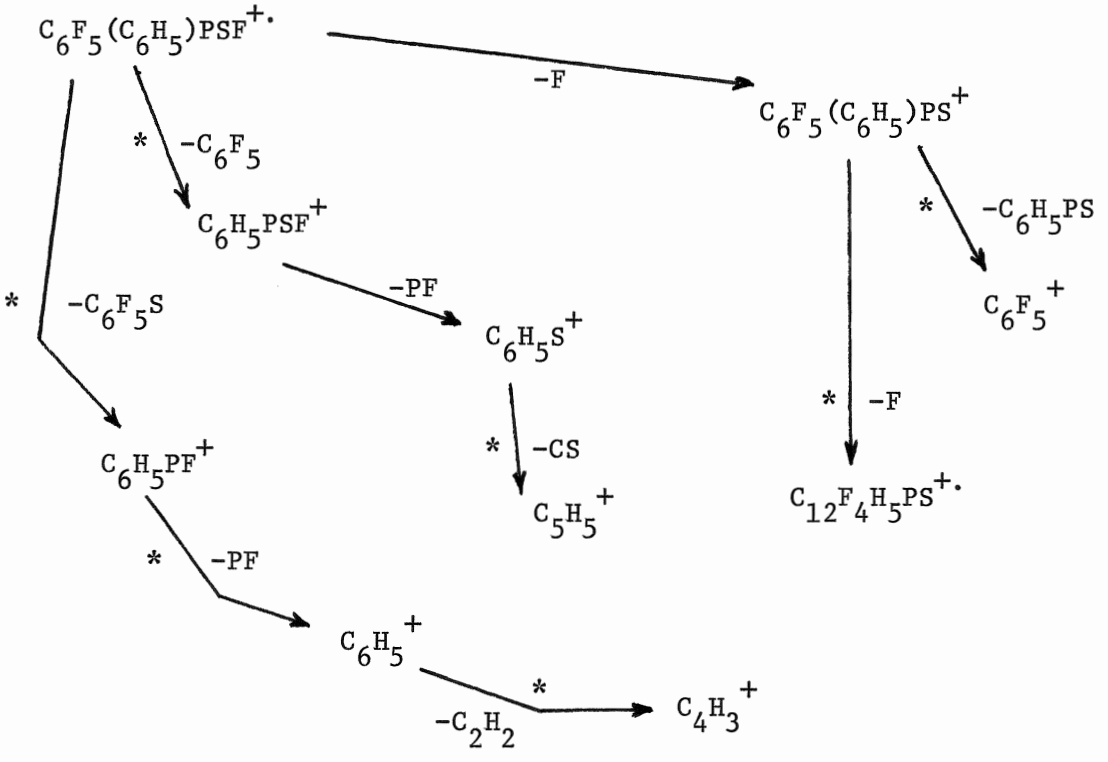
(C)


$C_6F_5(C_2H_5)PSF^{+\cdot}$
* -C_2H_4
$(C_6F_5)PHSF^{+\cdot}$
-C_6F_5
$HPSF^+$
-$C_2H_5PF_2$ *
$C_6F_4S^{+\cdot}$
*
-HPSF + PF_2
$C_5F_3^+$
* -HS
*
* -C_2H_4 + PSF
* -PSF
$C_6F_5PF^{+\cdot}$
-$HPSF_3$
-P *
-PF_3 *
$C_6F_3^+$
$C_6F_5H^{+\cdot}$
$C_6F_6^{+\cdot}$

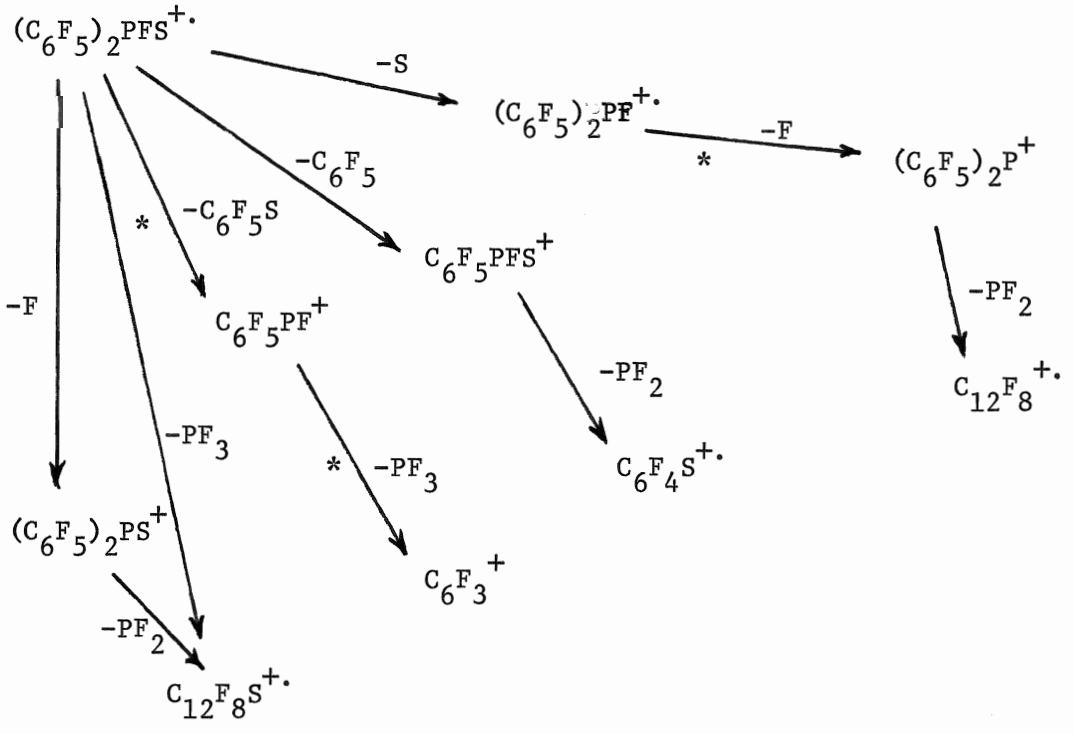
(D)


$C_6F_5(tC_4H_9)PSF^{+\cdot}$
-HS
$C_6F_5(C_4H_8)PF^+$
-CH_3
$C_6F_5(C_3H_6)PFS^+$
-C_4H_9S
$C_6F_5PF^+$
-C_6F_5PFS
$C_4H_9^+$

(E)


$C_6F_5(C_6H_5)PSF^{+\cdot}$
-F
$C_6F_5(C_6H_5)PS^+$
* $-C_6F_5$
$C_6H_5PSF^+$
* $-C_6H_5PS$
$C_6F_5^+$
-PF
* $-C_6F_5S$
$C_6H_5S^+$
* -F
* -CS
$C_5H_5^+$
$C_{12}F_4H_5PS^{+\cdot}$
$C_6H_5PF^+$
* -PF
$C_6H_5^+$
*
$-C_2H_2$
$C_4H_3^+$

(F)


$(C_6F_5)_2PFS^{+\cdot}$
-S
$(C_6F_5)_2PF^{+\cdot}$
-F
*
$(C_6F_5)_2P^+$
$-C_6F_5$
* $-C_6F_5S$
$C_6F_5PFS^+$
-F
$C_6F_5PF^+$
$-PF_2$
$-PF_2$
$C_{12}F_8^{+\cdot}$
$-PF_3$
* $-PF_3$
$C_6F_4S^{+\cdot}$
$(C_6F_5)_2PS^+$
$C_6F_3^+$
$-PF_2$
$C_{12}F_8S^{+\cdot}$

(G)

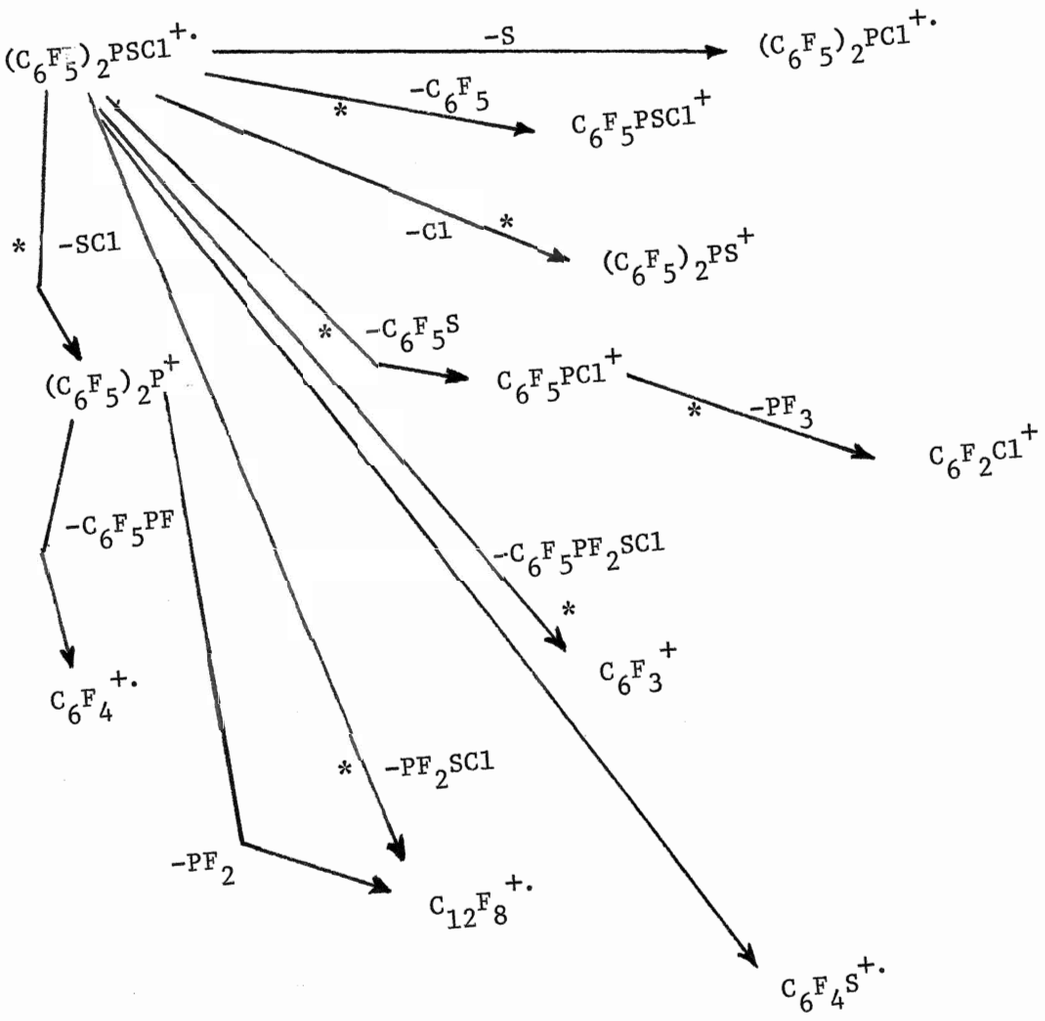

$(C_6F_5)_2PSCl^{+\cdot}$
-S
$(C_6F_5)_2PCl^{+\cdot}$
*
$-C_6F_5$
$C_6F_5PSCl^+$
-Cl
*
$(C_6F_5)_2PS^+$
*
-SCl
$(C_6F_5)_2P^+$
*
$-C_6F_5S$
$C_6F_5PCl^+$
*
$-PF_3$
$C_6F_2Cl^+$
$-C_6F_5PF$
$-C_6F_5PF_2SCl$
*
$C_6F_3^+$
$C_6F_4^{+\cdot}$
*
$-PF_2SCl$
$-PF_2$
$C_{12}F_8^{+\cdot}$
$C_6F_4S^{+\cdot}$

Figure 22
The Mass Spectrum
of $(C_6H_5)_2P(O)F$
at 70 eV

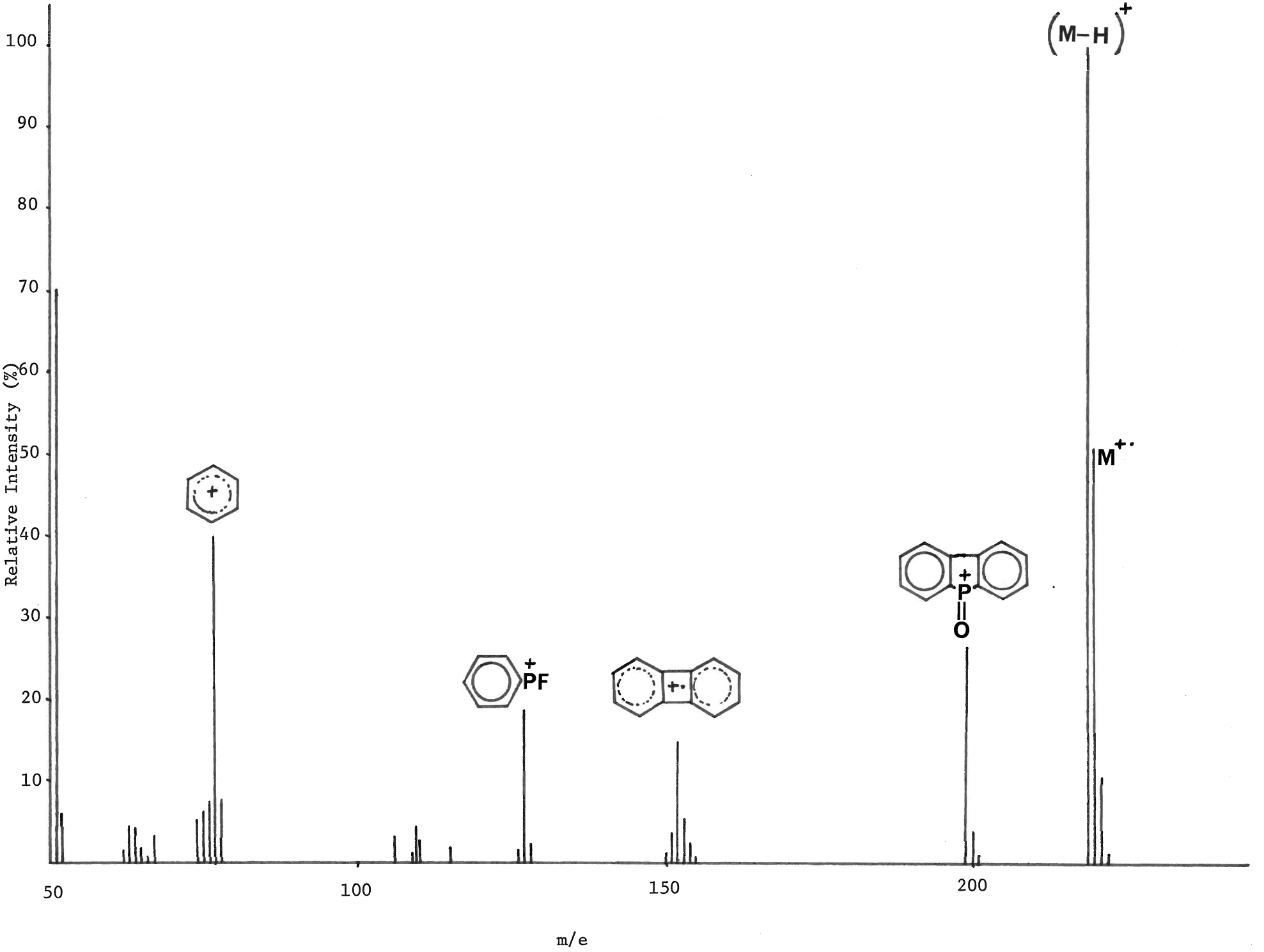

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
m/e
(M–H)+
M+·
PF+
P
O

Figure 23
The Mass Spectrum
of $(C_6F_5)(CH_3)P(O)F$
at 70 eV

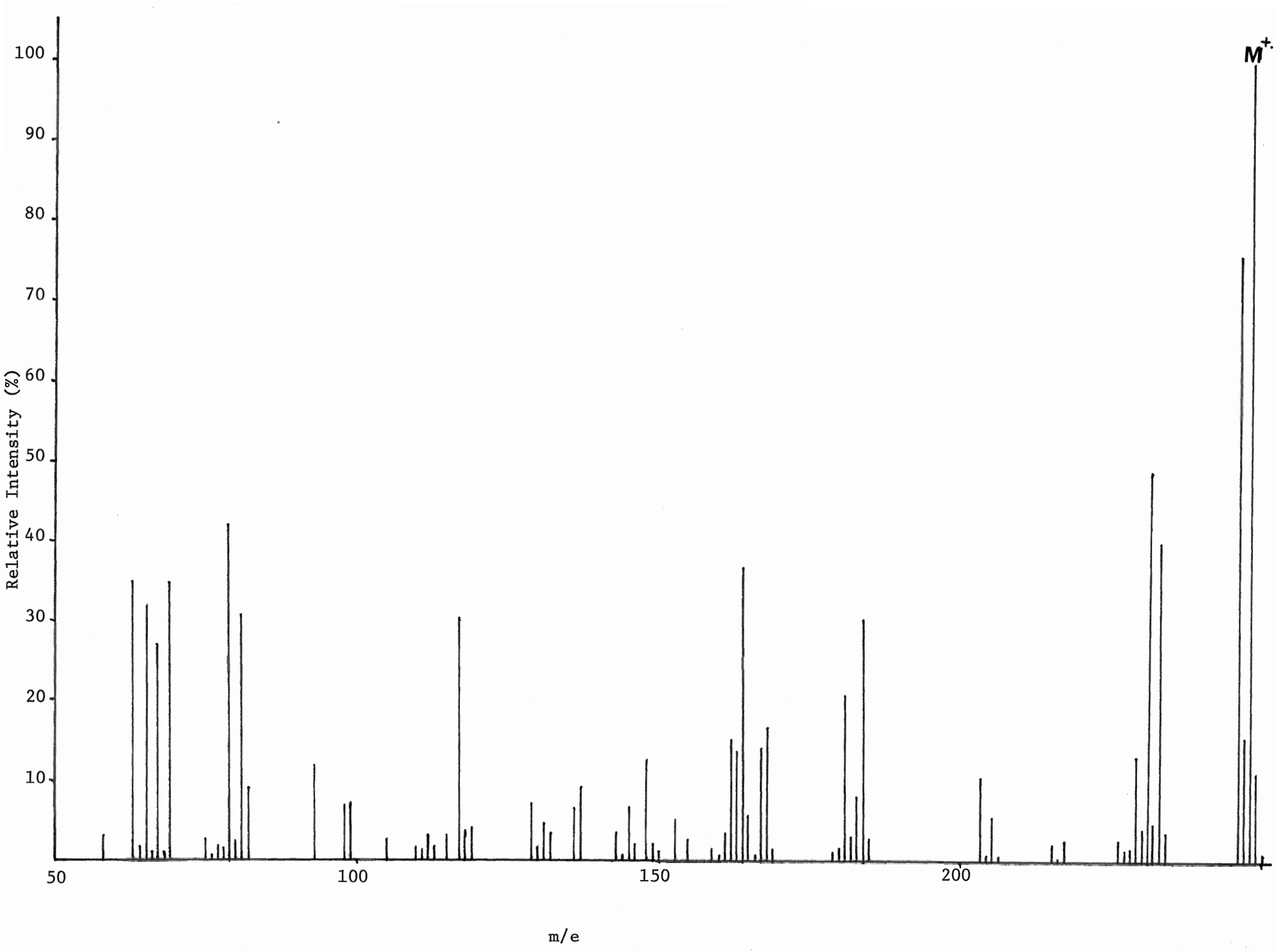

M+.
Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
m/e

Figure 24
The Mass Spectrum
of $(C_6F_5)(t\text{-}C_4H_9)P(O)F$
at 70 eV

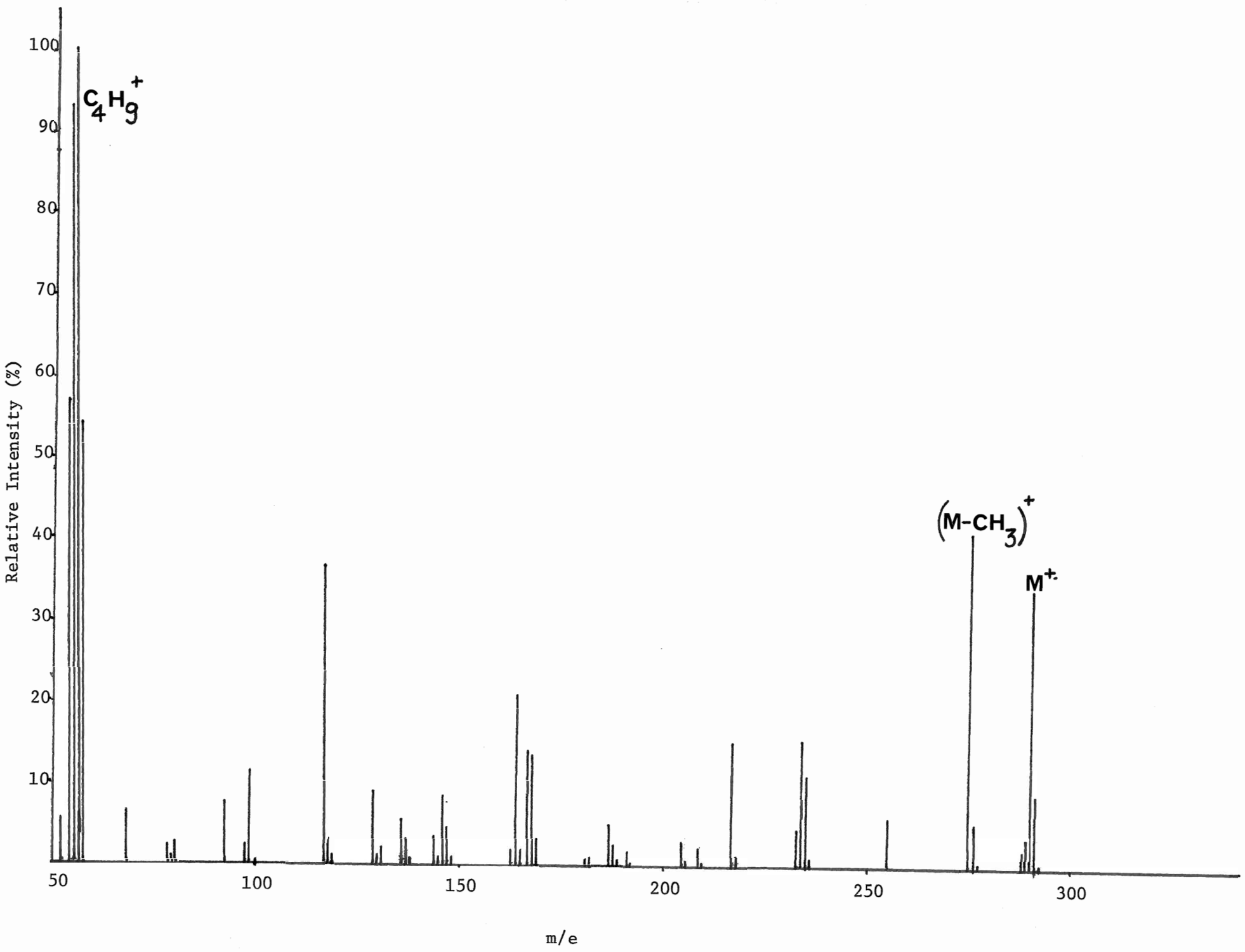

$C_4H_9^+$
$(M-CH_3)^+$
$M^{+\cdot}$
Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
m/e

Figure 25
The Mass Spectrum
of $(C_6F_5)(C_6H_5)P(O)F$
at 70 eV

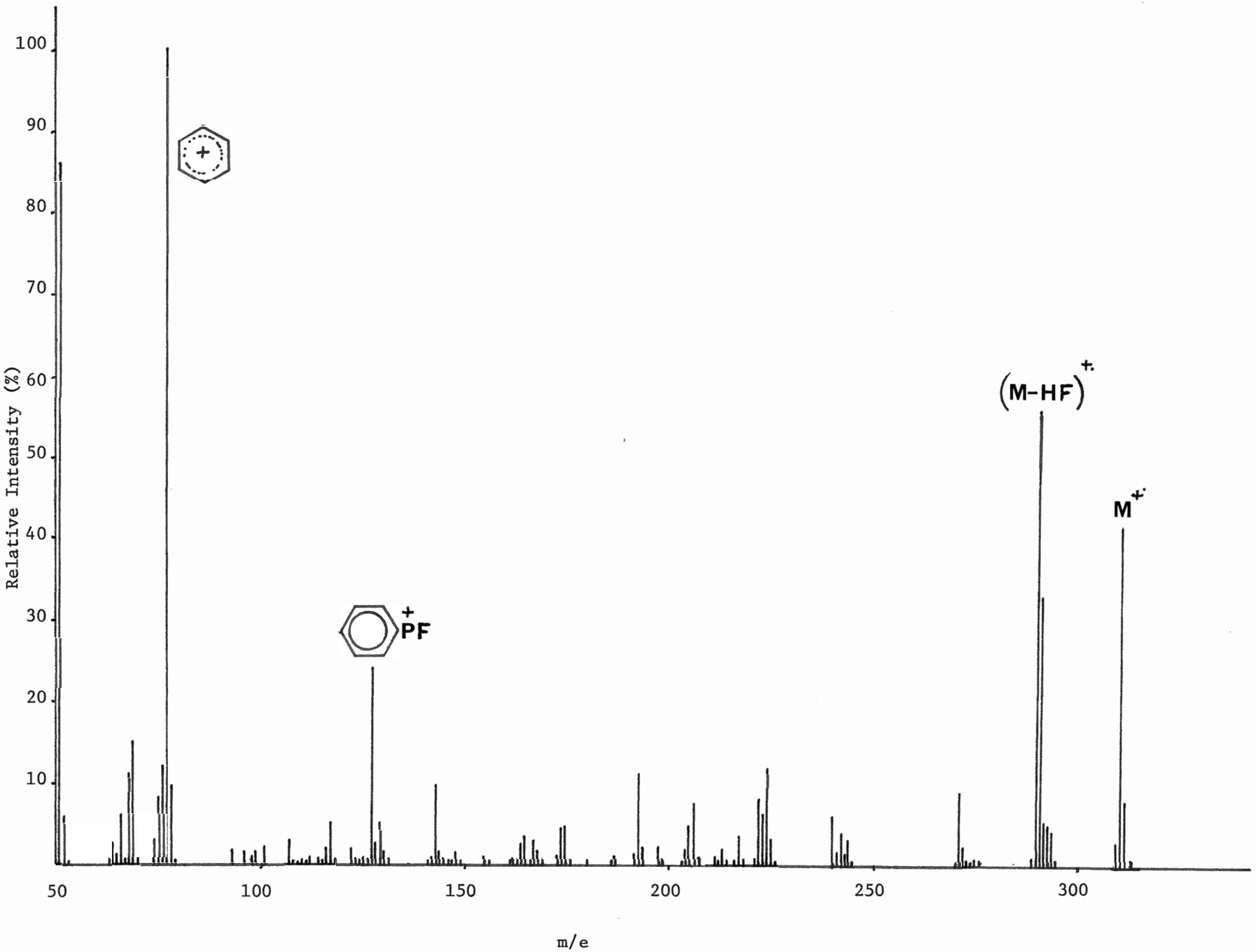
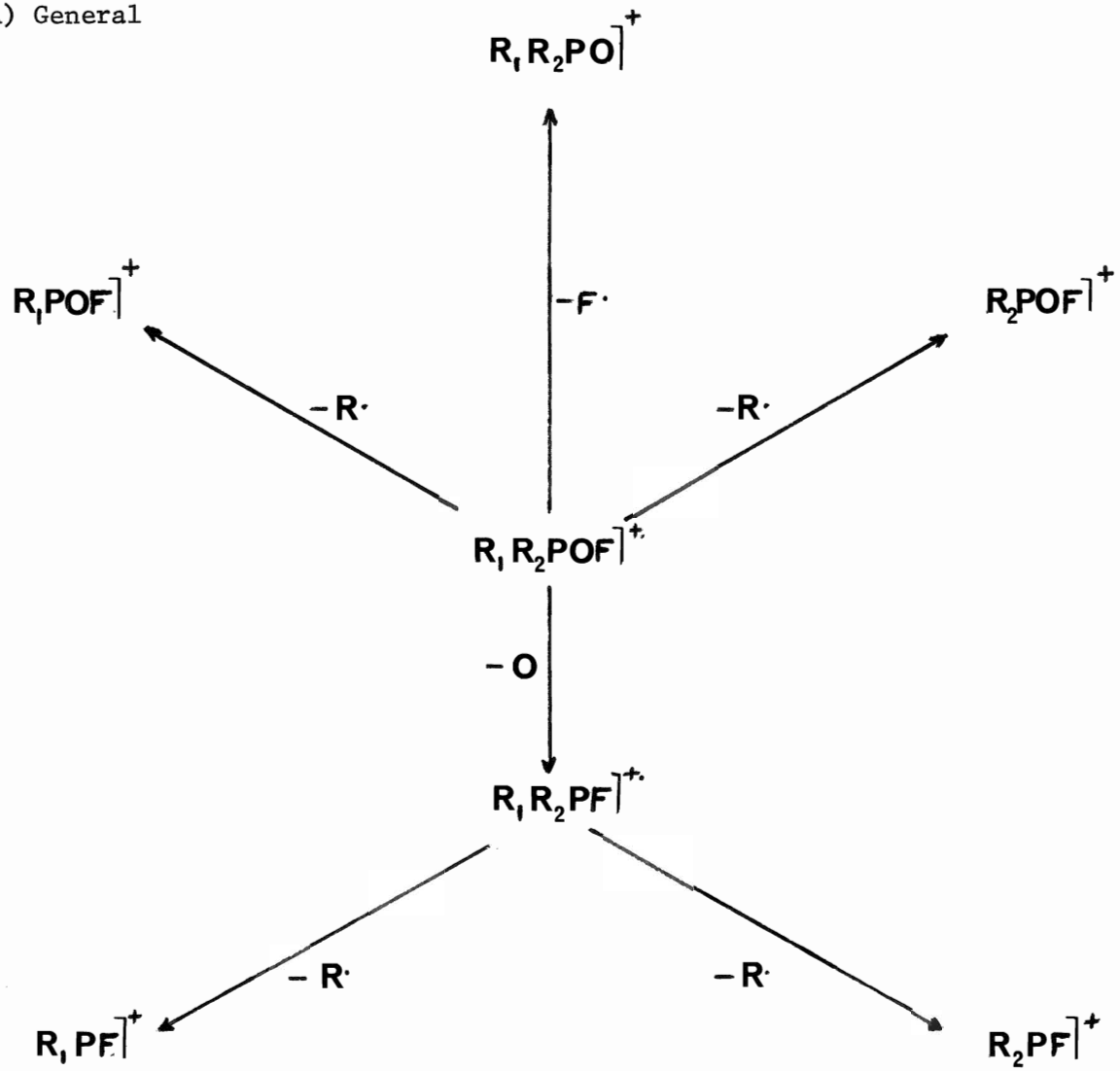

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
m/e
(M-HF)+·
M+·
+
PF

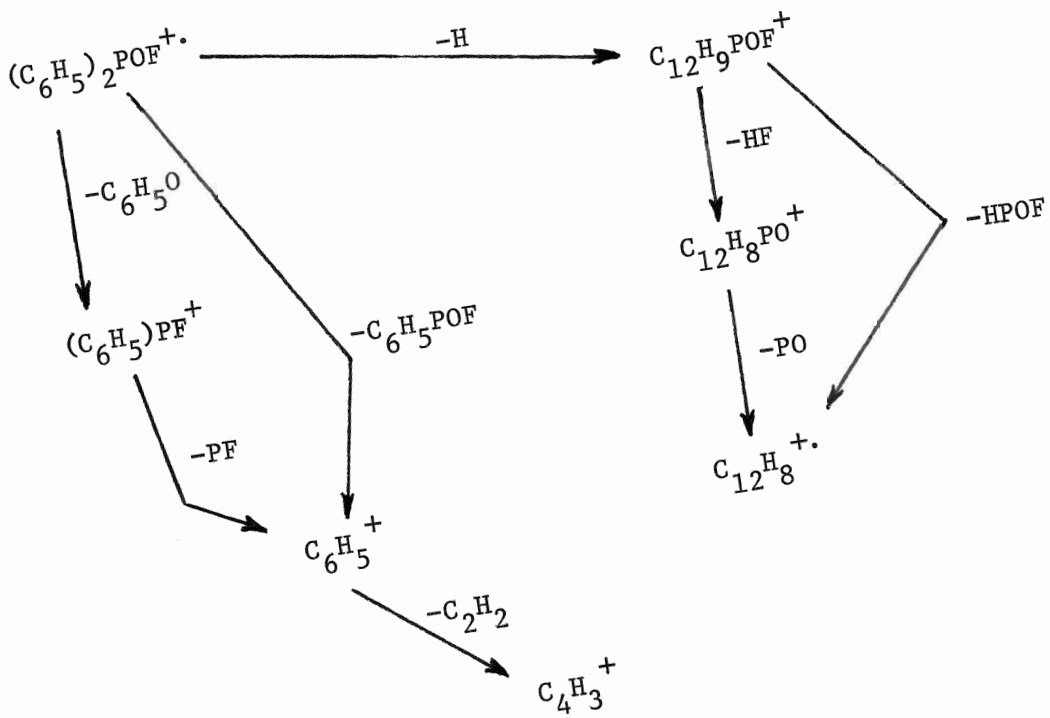
Figure 26
Fragmentation Schemes
for the series RR'P(O)F

(A) General
(B) R = C_6H_5, R' = C_6H_5
(C) R = C_6F_5, R' = CH_3
(D) R = " , R' = t-C_4H_9
(E) R = " , R' = C_6H_5

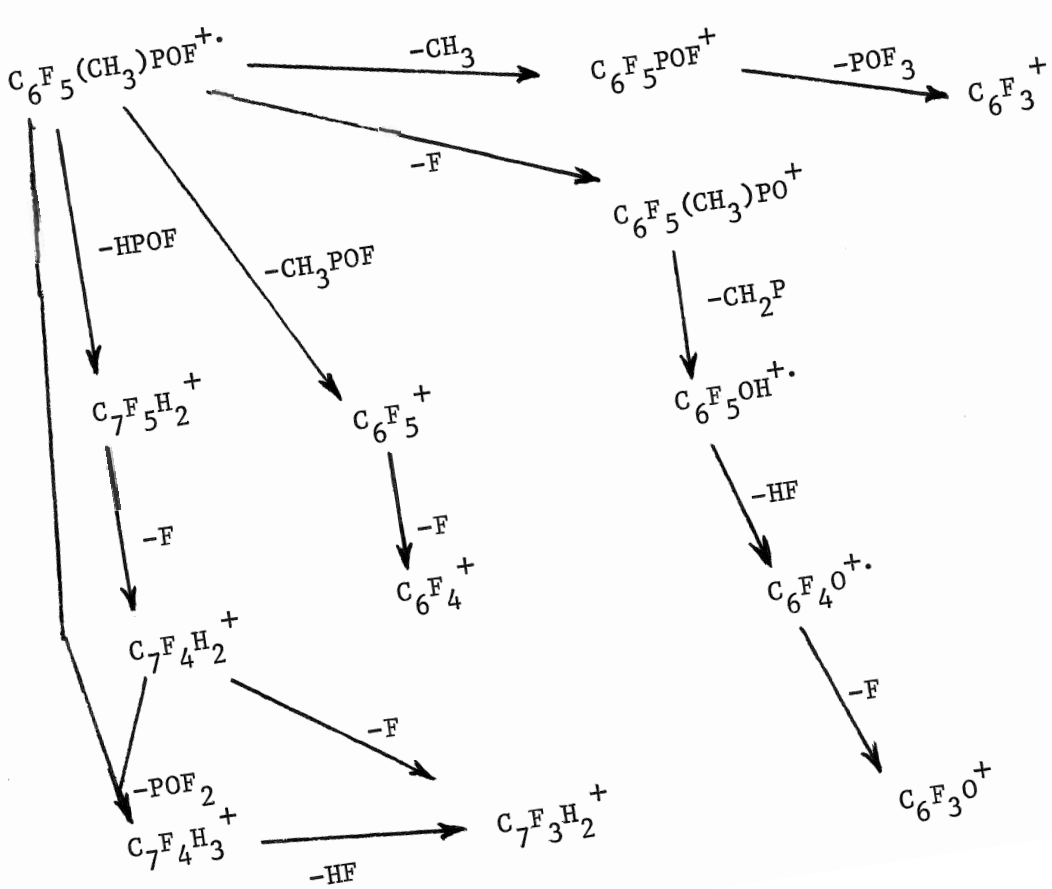
(A) General


$R_1R_2PO]^+$
$R_1POF]^+$
$R_2POF]^+$
$-F\cdot$
$-R\cdot$
$-R\cdot$
$R_1R_2POF]^{+\cdot}$
$-O$
$R_1R_2PF]^{+\cdot}$
$-R\cdot$
$-R\cdot$
$R_1PF]^+$
$R_2PF]^+$

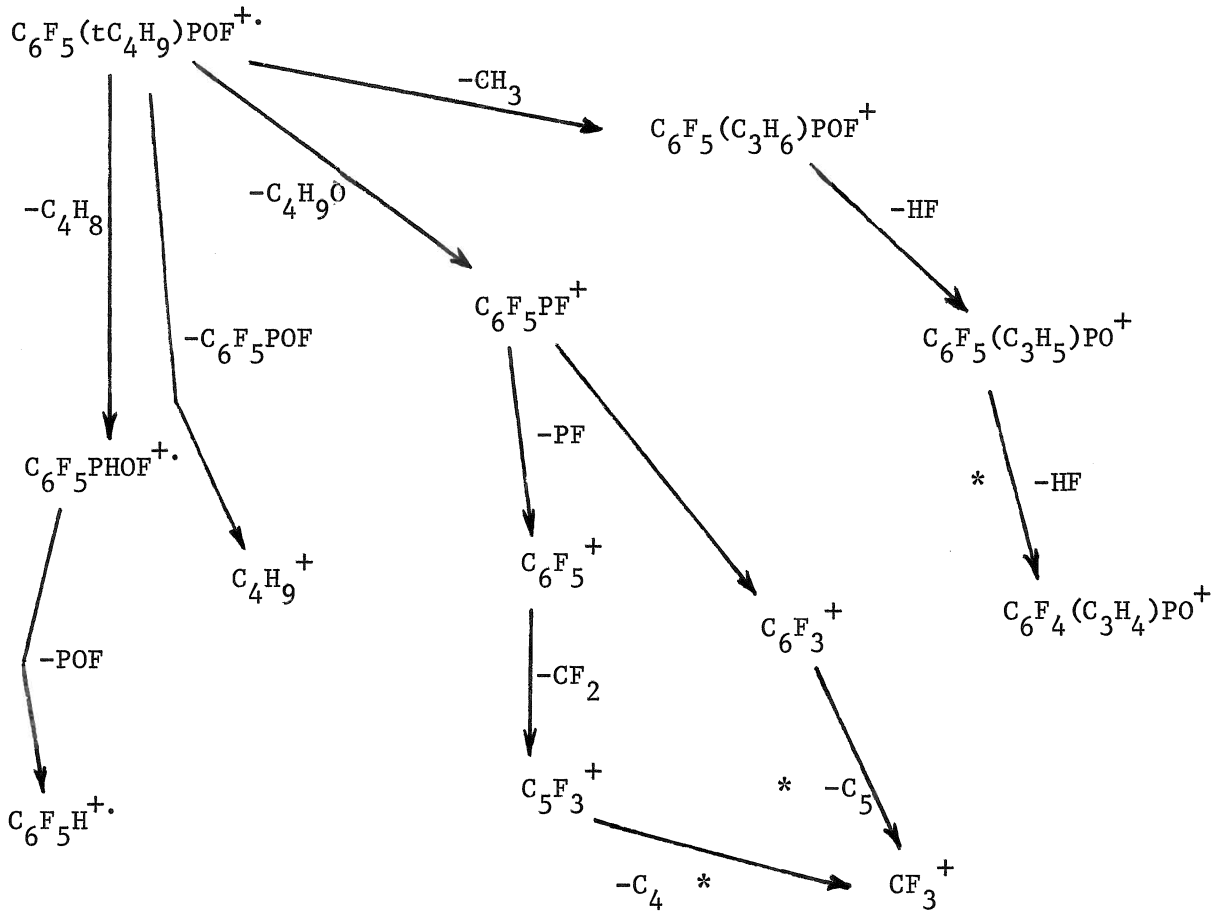
(B)


$(C_6H_5)_2POF^{+\cdot}$
-H
$C_{12}H_9POF^+$
$-C_6H_5O$
-HF
-HPOF
$C_{12}H_8PO^+$
$(C_6H_5)PF^+$
$-C_6H_5POF$
-PO
-PF
$C_{12}H_8^{+\cdot}$
$C_6H_5^+$
$-C_2H_2$
$C_4H_3^+$

(C)


$C_6F_5(CH_3)POF^{+\cdot}$
$-CH_3$
$C_6F_5POF^+$
$-POF_3$
$C_6F_3^+$
-F
$C_6F_5(CH_3)PO^+$
-HPOF
$-CH_3POF$
$-CH_2P$
$C_7F_5H_2^+$
$C_6F_5^+$
$C_6F_5OH^{+\cdot}$
-F
-F
-HF
$C_6F_4^+$
$C_6F_4O^{+\cdot}$
$C_7F_4H_2^+$
-F
-F
$-POF_2$
$C_7F_4H_3^+$
$C_7F_3H_2^+$
$C_6F_3O^+$
-HF

(D)


$C_6F_5(tC_4H_9)POF^{+\cdot}$
$-CH_3$
$C_6F_5(C_3H_6)POF^+$
$-C_4H_8$
$-C_4H_9O$
$-HF$
$C_6F_5PF^+$
$C_6F_5(C_3H_5)PO^+$
$-C_6F_5POF$
$-PF$
$C_6F_5PHOF^{+\cdot}$
*
$-HF$
$C_4H_9^+$
$C_6F_5^+$
$C_6F_4(C_3H_4)PO^+$
$C_6F_3^+$
$-POF$
$-CF_2$
$C_6F_5H^{+\cdot}$
$C_5F_3^+$
*
$-C_5$
$-C_4$
*
CF_3^+

(E)

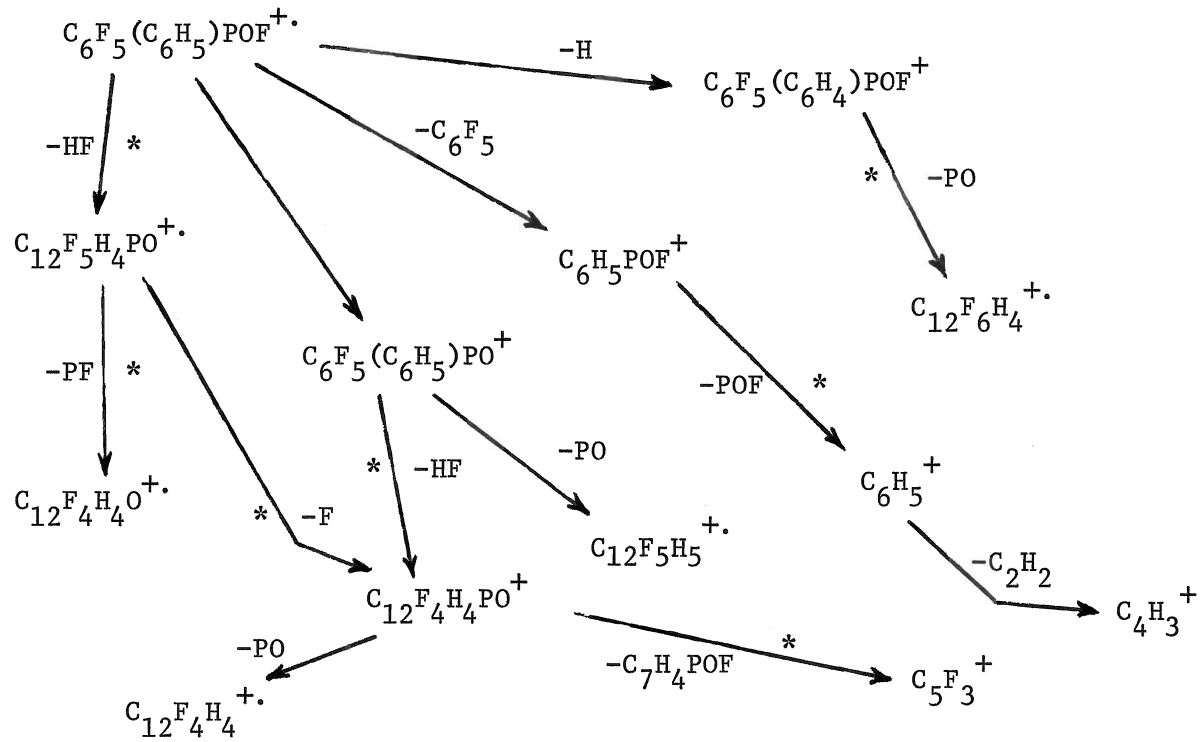

$C_6F_5(C_6H_5)POF^{+\cdot}$
$-H$
$C_6F_5(C_6H_4)POF^+$
$-HF$
*
$-C_6F_5$
*
$-PO$
$C_{12}F_5H_4PO^{+\cdot}$
$C_6H_5POF^+$
$C_{12}F_6H_4^{+\cdot}$
$-PF$
*
$C_6F_5(C_6H_5)PO^+$
$-POF$
*
*
$-HF$
$-PO$
$C_6H_5^+$
$C_{12}F_4H_4O^{+\cdot}$
*
$-F$
$C_{12}F_5H_5^{+\cdot}$
$-C_2H_2$
$C_{12}F_4H_4PO^+$
$C_4H_3^+$
$-PO$
$-C_7H_4POF$
*
$C_5F_3^+$
$C_{12}F_4H_4^{+\cdot}$

Figure 27
The Mass Spectrum
of $(C_6F_5)_3PF_2$
at 70 eV

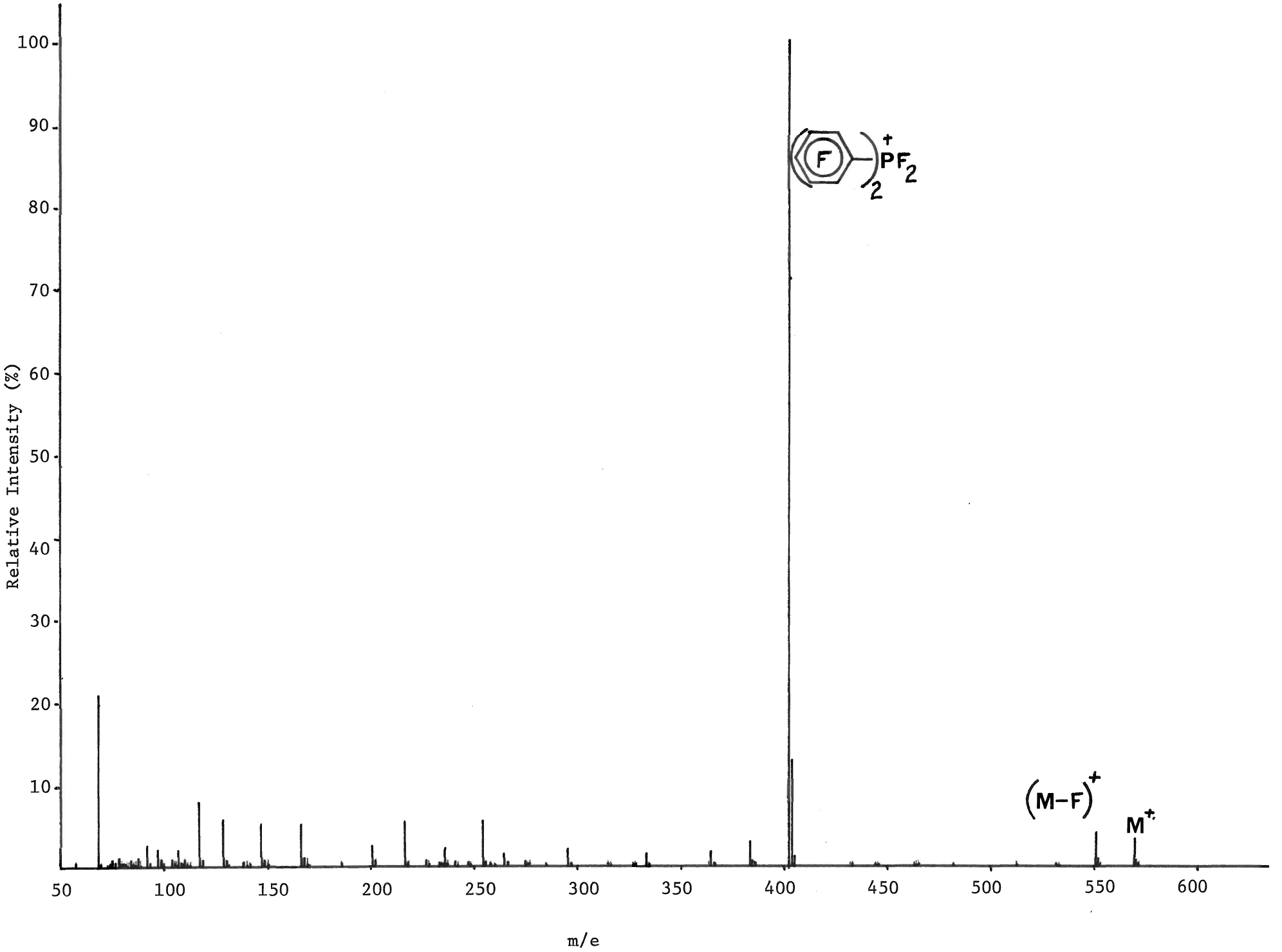

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
450
500
550
600
m/e
F
PF2
2
(M-F)+
M+.

Figure 28
The Mass Spectrum
of $(C_6F_5)_2(C_2H_5S)PF_2$
at 70 eV

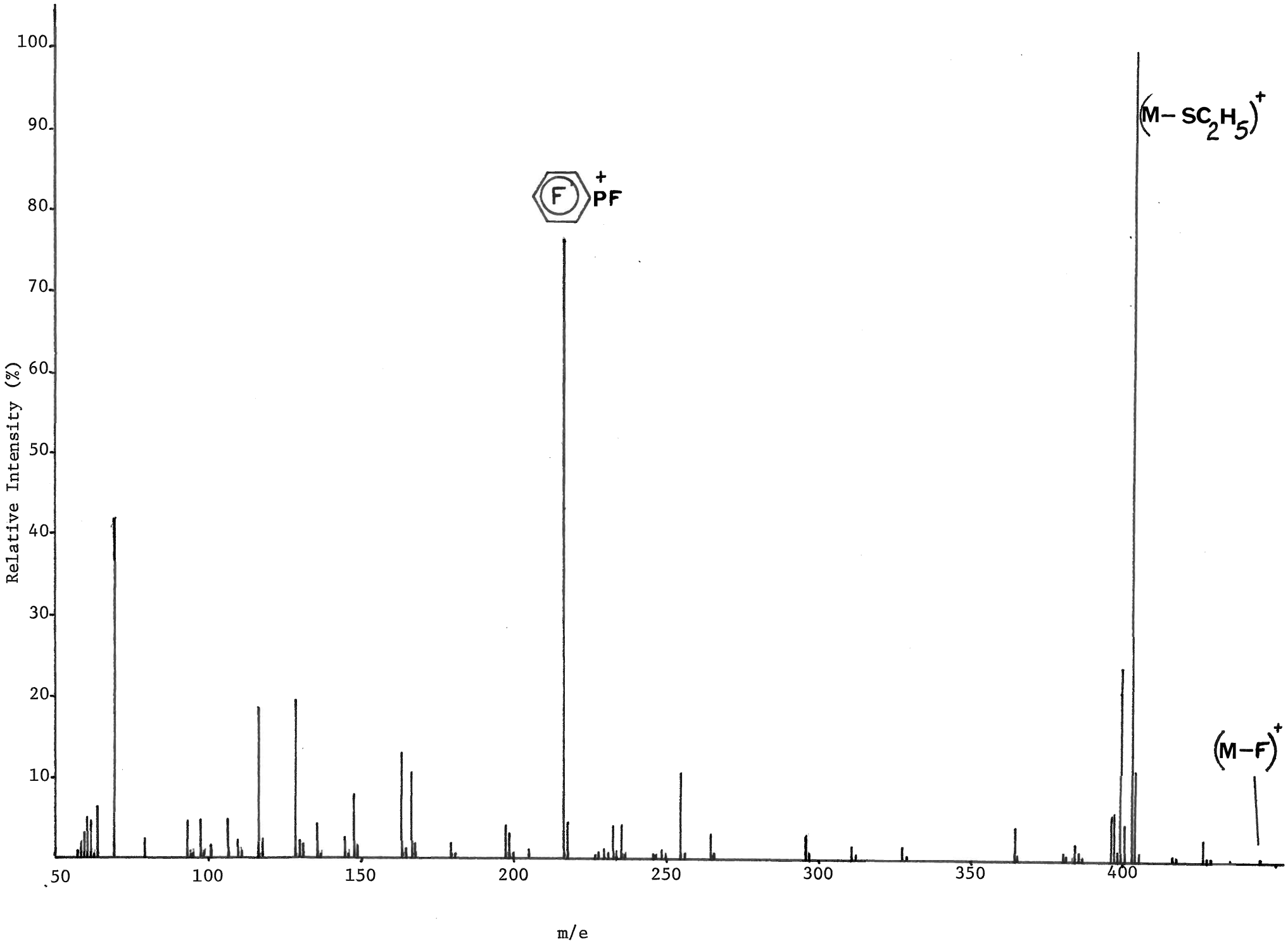
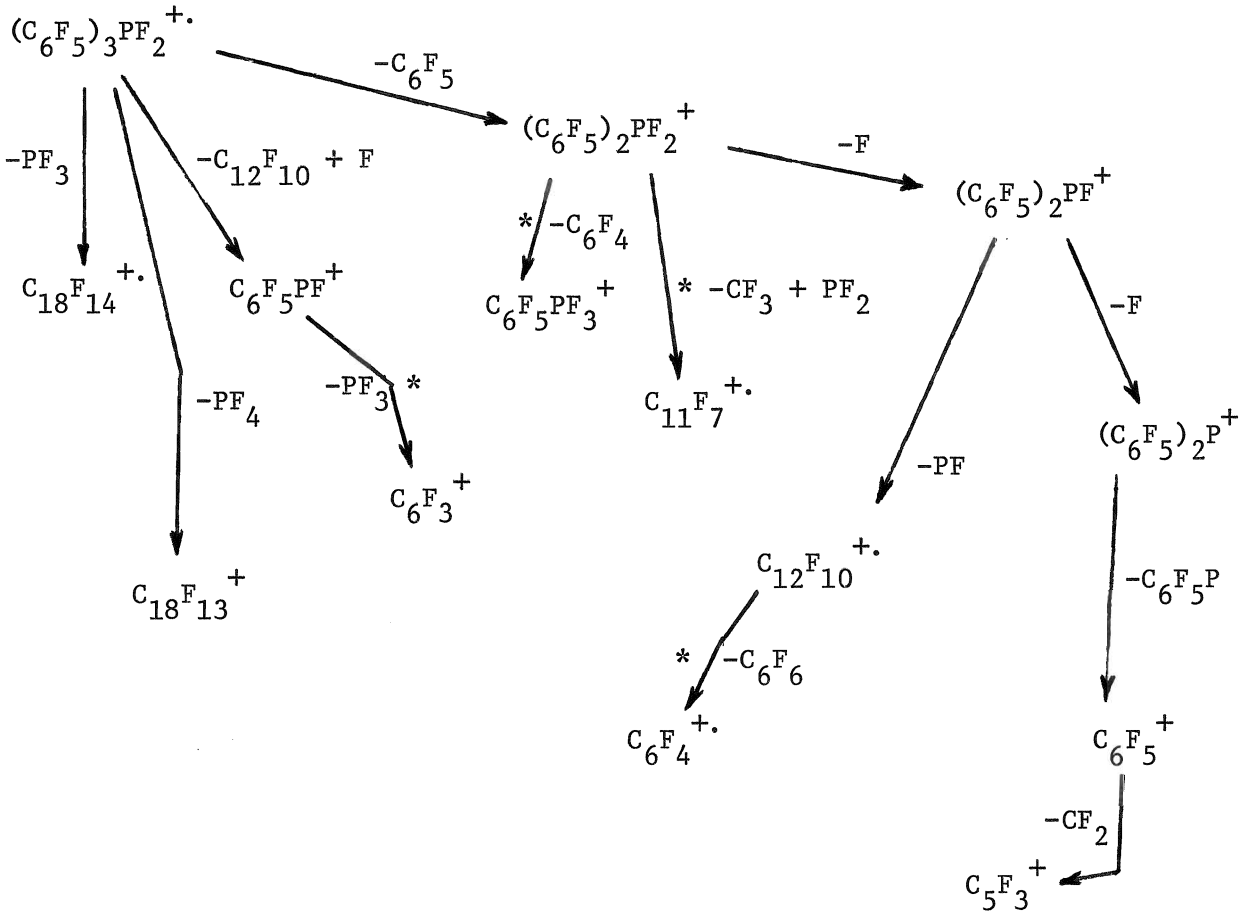

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
m/e
F
+
PF
(M− SC2H5)+
(M−F)+

Figure 29
Fragmentation Schemes
for

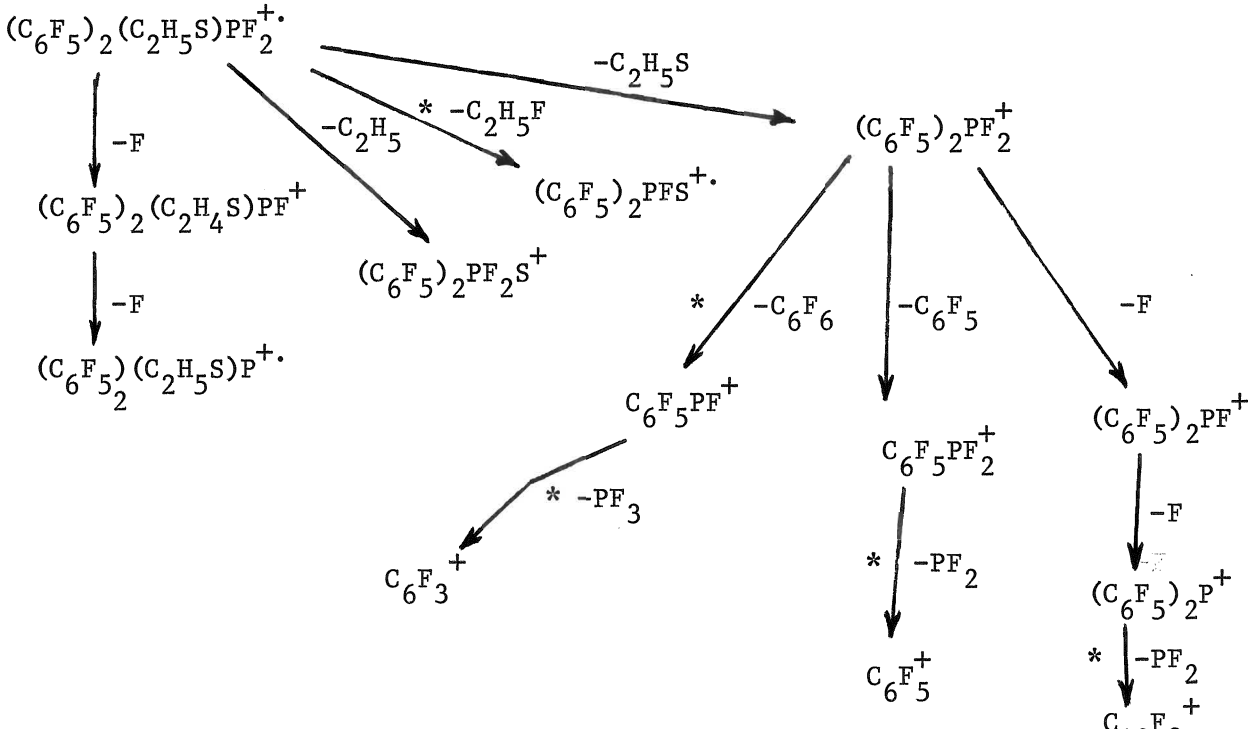
(A) $(C_6F_5)_3PF_2$

(B) $(C_6F_5)_2(C_2H_5S)PF_2$

(A)


$(C_6F_5)_3PF_2^{+\cdot}$
$-C_6F_5$
$(C_6F_5)_2PF_2^{+}$
$-PF_3$
$-C_{12}F_{10}$ + F
$-F$
$(C_6F_5)_2PF^{+}$
$C_{18}F_{14}^{+\cdot}$
$C_6F_5PF^{+}$
*$-C_6F_4$
$C_6F_5PF_3^{+}$
* $-CF_3$ + PF_2
$-F$
$-PF_4$
$-PF_3$ *
$C_{11}F_7^{+\cdot}$
$-PF$
$(C_6F_5)_2P^{+}$
$C_6F_3^{+}$
$C_{18}F_{13}^{+}$
$C_{12}F_{10}^{+\cdot}$
$-C_6F_5P$
* $-C_6F_6$
$C_6F_4^{+\cdot}$
$C_6F_5^{+}$
$-CF_2$
$C_5F_3^{+}$

(B)


$(C_6F_5)_2(C_2H_5S)PF_2^{+\cdot}$
$-C_2H_5S$
$-F$
$-C_2H_5$
* $-C_2H_5F$
$(C_6F_5)_2PF_2^{+}$
$(C_6F_5)_2(C_2H_4S)PF^{+}$
$(C_6F_5)_2PFS^{+\cdot}$
$(C_6F_5)_2PF_2S^{+}$
$-F$
$(C_6F_5)_2(C_2H_5S)P^{+\cdot}$
* $-C_6F_6$
$-C_6F_5$
$-F$
$C_6F_5PF^{+}$
$C_6F_5PF_2^{+}$
$(C_6F_5)_2PF^{+}$
* $-PF_3$
$C_6F_3^{+}$
* $-PF_2$
$-F$
$C_6F_5^{+}$
$(C_6F_5)_2P^{+}$
* $-PF_2$

$$(C_6F_5)_2P\text{-}SC_2H_5\rceil^+ \not\longrightarrow (C_6F_5)_2P(S)C_2H_5\rceil^+$$

but there is evidence for operation of the original processes following loss of C_2H_5 from the parent ion. Fragments corresponding to $C_6F_5S^+$ and $C_6F_4S^+$ are observed in low abundance.

Again, considerable metastable ion support indicates the operation of halogen transfer sequences as depicted by the following transitions.

$$(C_6F_5)_2P\rceil^+ \xrightarrow{-PF_2} C_{12}F_8\rceil^+$$

m*obs 240.1
m*calc 240.04

(m/e 365, 4.3% (m/e 296, 3.1%

$$C_6F_5PF\rceil^+ \xrightarrow{-PF_3} C_6F_3\rceil^+$$

m*obs 76.7
m*calc 76.69

(m/e 217, 16.9%) (m/e 129, 4.6%

2 (a) The Mass Spectra of $C_6F_5M(CH_3)_2$ M = N,P,As

The partial mass spectra of these compounds are shown in Table 10 and the mass spectra and postulated fragmentation schemes in Figures 30 - 33.

Ambiguities concerning the identity of some of the fragment ions in the spectrum of the phosphine were resolved by detection of similar transitions in the spectra of both amine and arsine as well as high resolution support. The appearance, and high abundance of the C_7F_5MH species is rather interesting since one might expect consecutive loss of methyl radicals as the preferred breakdown pathway. Indeed, the formation of this ion is reminiscent of tendencies observed for N,N dimethyl aniline and trimethyl phosphine. In the latter case[6,7], loss of a methyl radical is the first step in fragmentation giving rise to the base peak $(CH_3)_2P^+$. The second largest peak in the spectrum corresponds to $CH_2 = \overset{+}{P} = CH_2$ being formed by loss of H_2 from the base ion. One can see definite analogies to the series of transitions leading to C_7F_5MH. The intensity of this ion is greatest for M = P>N>As. This trend can be rationalized in terms of more stable M^+ and $(M-H)^+$ ions in the spectrum of the amine and to weaker As-C bonds in the case of the arsine. The progressive weakening of M-C bonds which is seen in many groups in the periodic table as one descends the group is clearly demonstrated by the abundance of the parent ions for which M = N>P>As.

The high abundance of $(M-H)^+$ in the spectrum of the amine results from the normal alpha-cleavage demonstrated by alkyl amines. This mode of fragmentation is initiated by a radical site on nitrogen. Phosphorous and arsenic being "softer" atoms are poorer initiators due to their

" Text continues on page 77."

TABLE 10

PARTIAL MASS SPECTRA OF $C_6F_5M(CH_3)_2$

Ion$^+$	M = N	M = P	M = As
$(CH_3)_2MC_6F_5$	31.0	21.8	9.1
$C_2H_5MC_6F_5$	35.1	0.2	---
$CH_3MC_6F_5$	1.4	6.8	9.6
$HCMC_6F_5$	6.4	14.4	4.5
HMC_6F_5	1.4	1.2	0.4
MC_6F_5	2.4	0.2	2.2
MC_6F_4	0.2	0.4	0.7
MF_2	---	Masked by CF_3	2.0
$M(CH_3)_2$	0.1	0.9	Masked by C_4F_3
$M(CH_3)$	---	0.8	1.6
MCH_2	---	4.5	4.5
MF	---	Masked by CF_2	1.0
$C_7F_5H_2$	2.5	9.5	6.9
C_6F_5H	0.7	1.9	0.8
$C_7F_4H_3$	1.4	0.9	2.3
C_7F_4H	0.1	1.0	1.2
$C_7F_3H_3$	0.1	2.0	1.2
$C_7F_3H_2$	0.1	1.8	1.1
$C_6F_3H_2$	0.2	0.2	0.3
C_6F_5	1.5	0.1	---
$C_7H_5F_2$	0.1	1.8	2.4
$C_7H_3F_2$	0.1	1.1	0.3
C_7HF_2	---	1.1	0.3
$C_5H_3F_2$	0.3	0.2	---
C_6F_3	---	0.3	1.5
C_5F_2H	0.4	1.4	0.7
C_5F_3	0.6	0.9	---
C_4F_3	---	0.3	3.8
C_3F_3	0.2	1.1	0.6
C_3F_2H	0.1	1.5	0.8

Figure 30
The Mass Spectrum
of $(C_6F_5)N(CH_3)_2$
at 70 eV

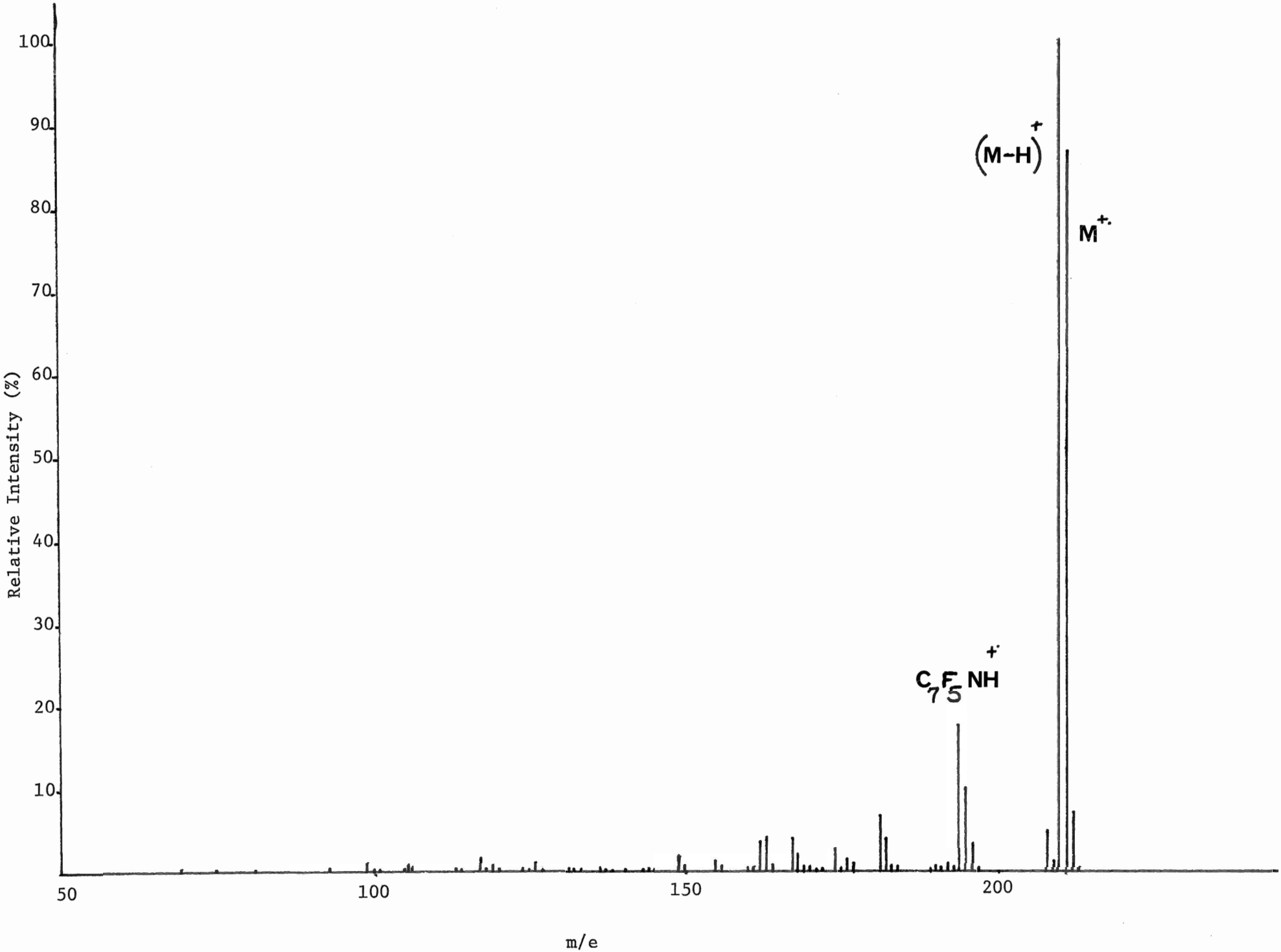

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
(M-H)+
M+.
C7F5NH+
50
100
150
200
m/e

Figure 31
The Mass Spectrum
of $(C_6F_5)P(CH_3)_2$
at 70 eV

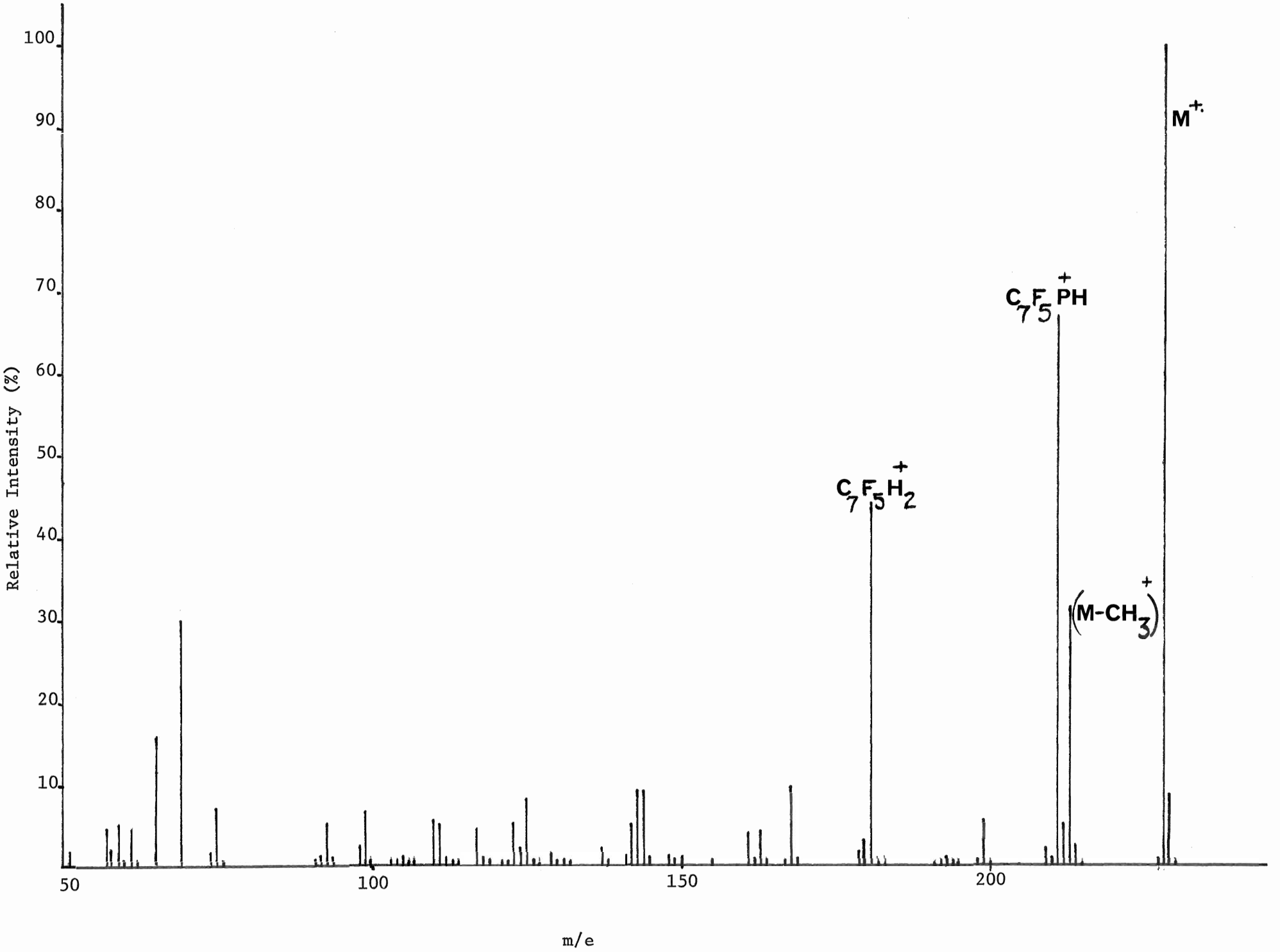

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
m/e
M+.
C7F5PH+
C7F5H2+
(M-CH3)+

Figure 32
The Mass Spectrum
of $(C_6F_5)As(CH_3)_2$
at 70 eV

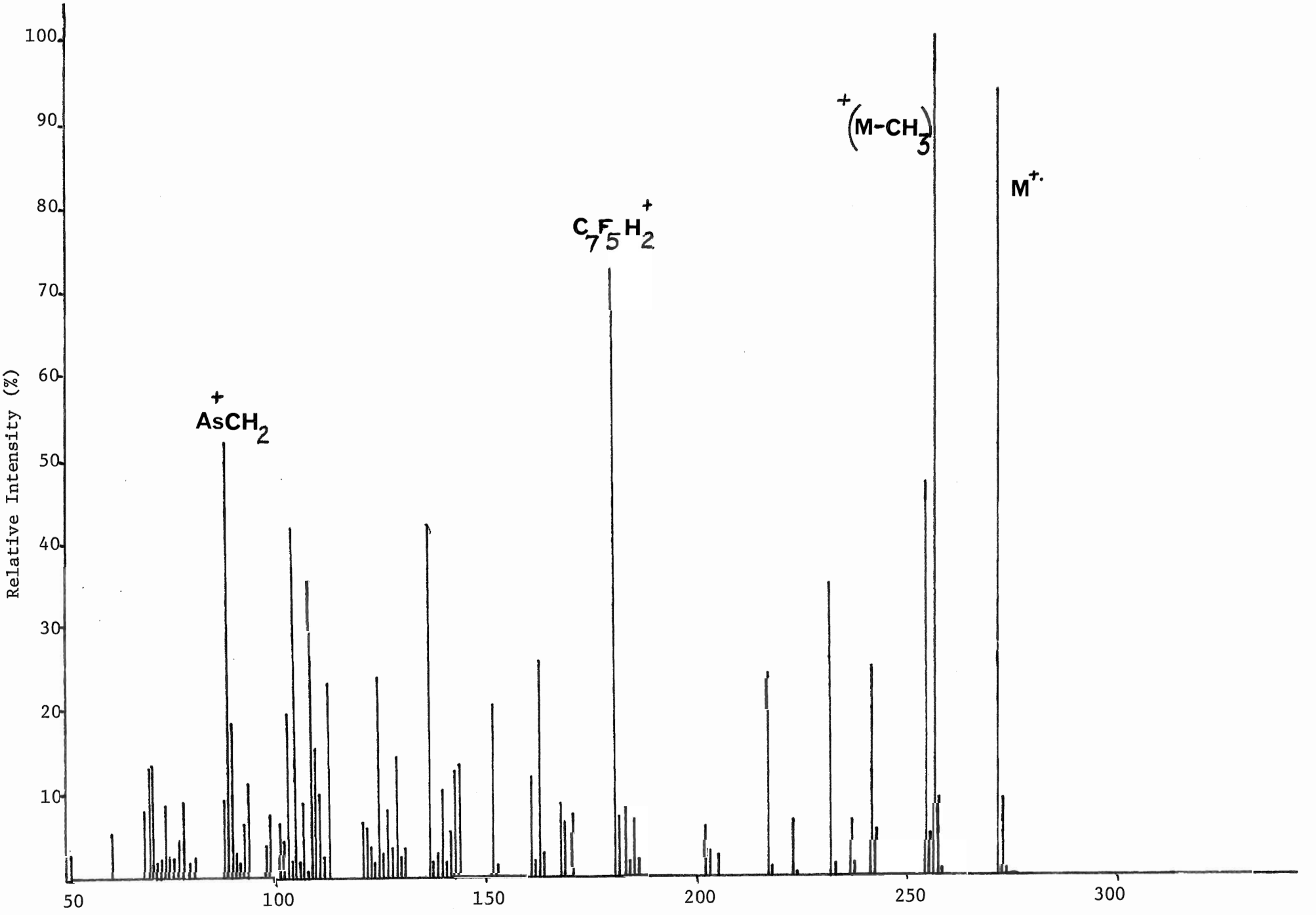
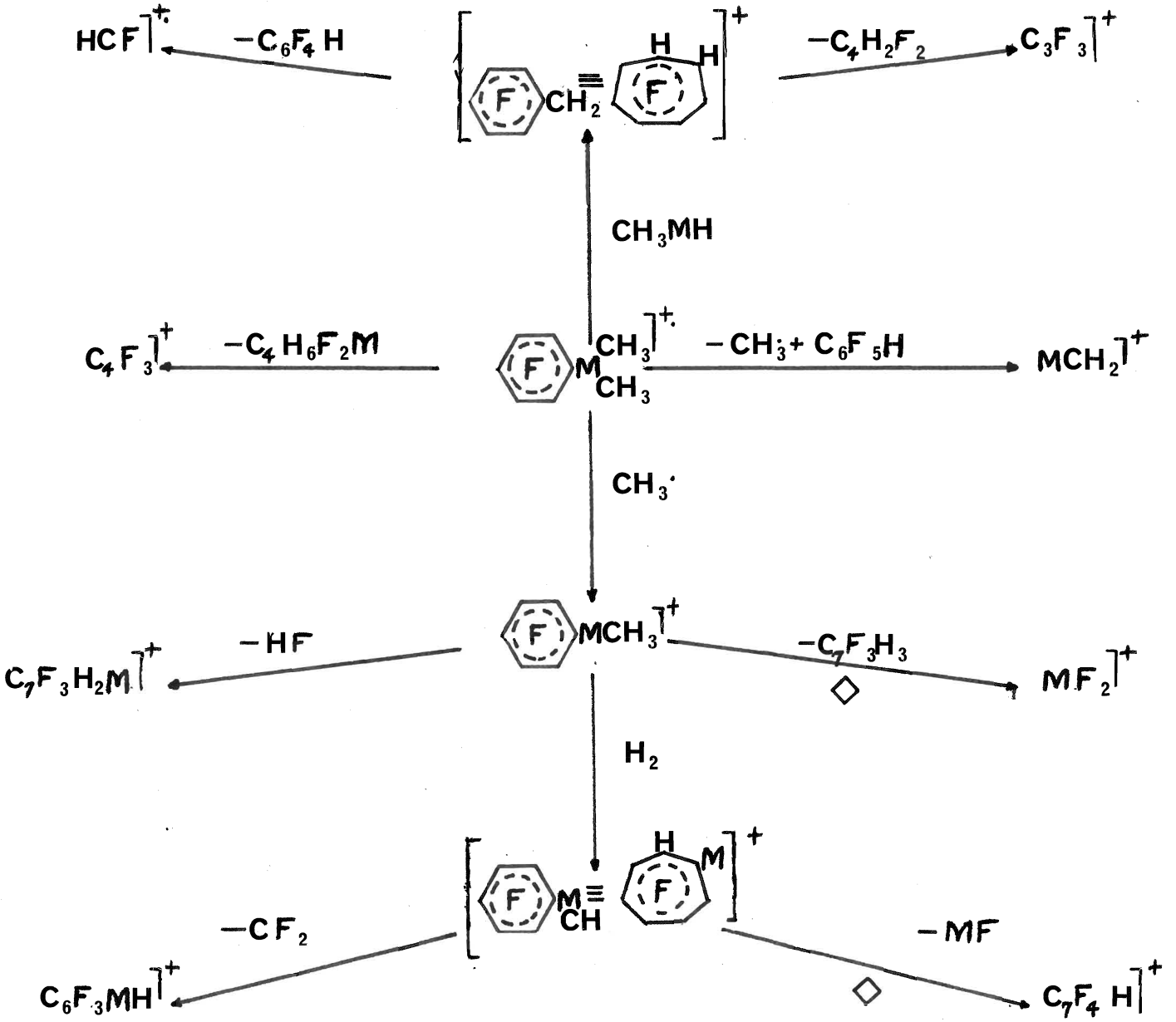

Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
$^{+}AsCH_2$
$C_7F_5H_2^{+}$
$^{+}(M-CH_3)$
$M^{+\cdot}$

Figure 33
Fragmentation Schemes
for the series $(C_6F_5)M(CH_3)_2$

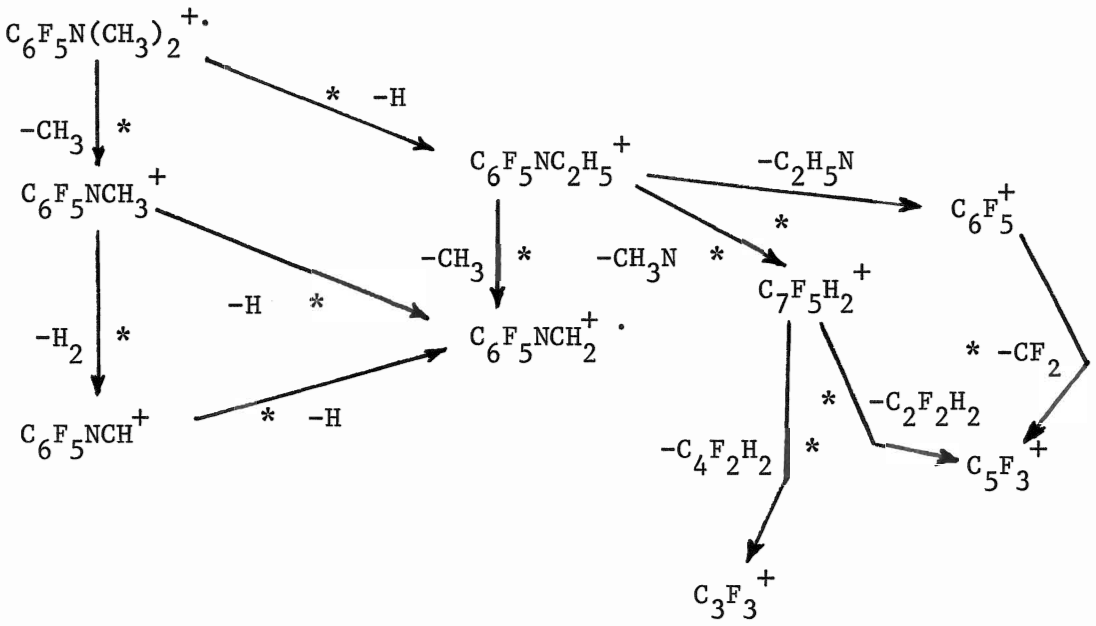
(A) General
(B) M = N
(C) M = P
(D) M = As

(A) General

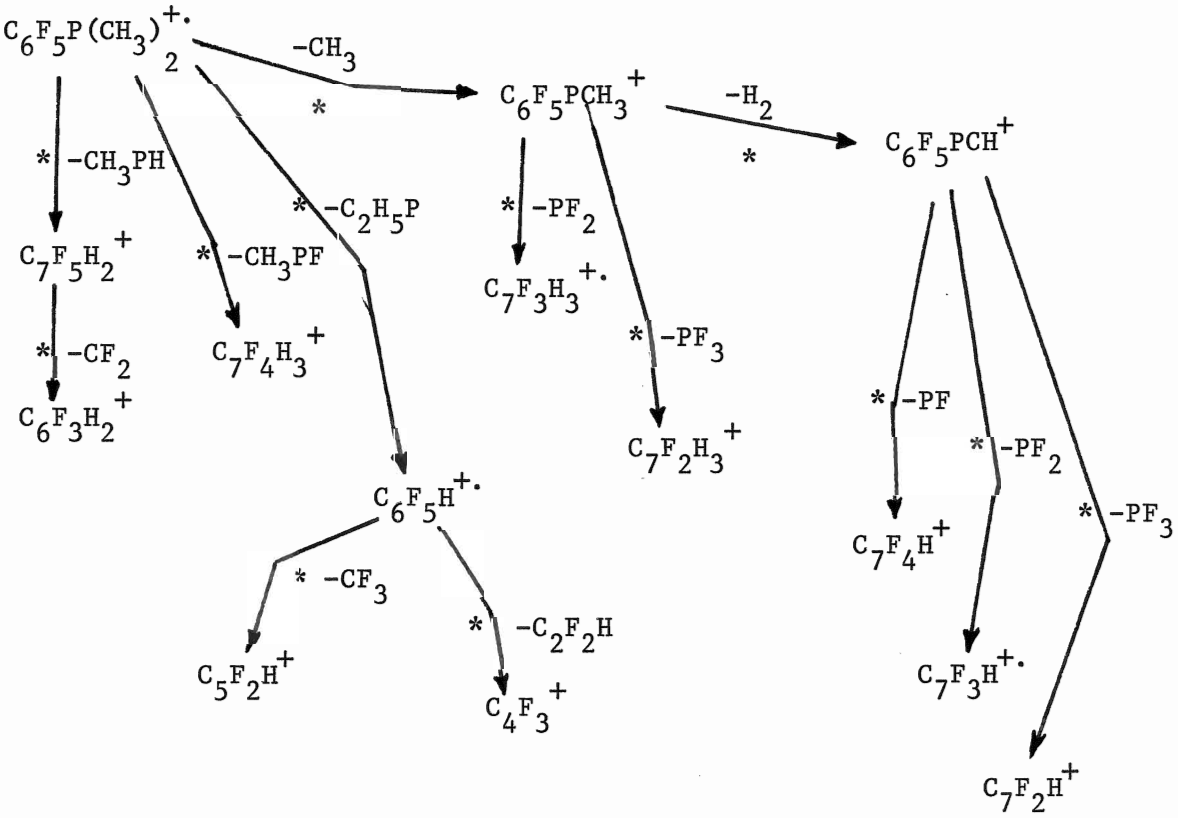


◇ Not observed for M = N

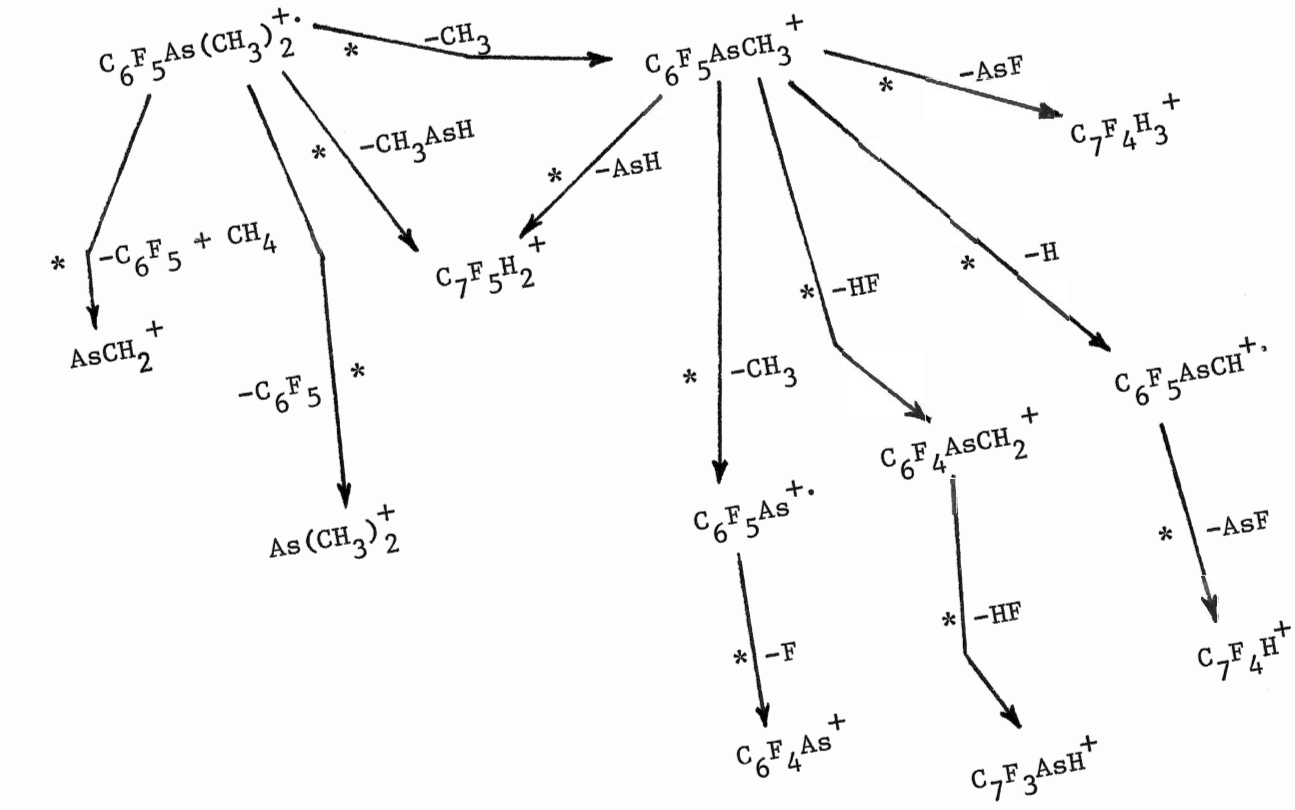
(B)


$C_6F_5N(CH_3)_2^{+\cdot}$
* -H
$C_6F_5NC_2H_5^+$
$-C_2H_5N$
$C_6F_5^+$
$-CH_3$ *
$C_6F_5NCH_3^+$
-H *
$-CH_3$ *
$-CH_3N$ *
$C_7F_5H_2^+$
$-H_2$ *
$C_6F_5NCH_2^+$ ·
* $-CF_2$
$C_6F_5NCH^+$
* -H
* $-C_2F_2H_2$
$-C_4F_2H_2$ *
$C_5F_3^+$
$C_3F_3^+$

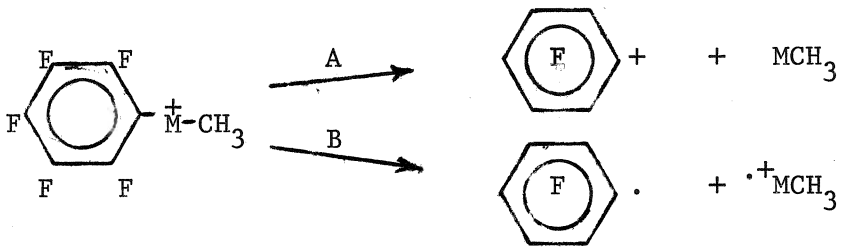
(C)


$C_6F_5P(CH_3)_2^{+\cdot}$
$-CH_3$
*
$C_6F_5PCH_3^+$
$-H_2$
*
$C_6F_5PCH^+$
* $-CH_3PH$
* $-C_2H_5P$
* $-PF_2$
$C_7F_5H_2^+$
* $-CH_3PF$
$C_7F_3H_3^{+\cdot}$
* $-PF_3$
$C_7F_4H_3^+$
* $-CF_2$
$C_7F_2H_3^+$
$C_6F_3H_2^+$
* -PF
* $-PF_2$
$C_6F_5H^{+\cdot}$
$C_7F_4H^+$
* $-PF_3$
* $-CF_3$
$C_7F_3H^{+\cdot}$
* $-C_2F_2H$
$C_5F_2H^+$
$C_4F_3^+$
$C_7F_2H^+$

(D)


$C_6F_5As(CH_3)_2^{+\cdot}$
$-CH_3$
$C_6F_5AsCH_3^+$
$-AsF$
$C_7F_4H_3^+$
$-CH_3AsH$
$-AsH$
$C_7F_5H_2^+$
$-C_6F_5 + CH_4$
$AsCH_2^+$
$-C_6F_5$
$As(CH_3)_2^+$
$-CH_3$
$-HF$
$-H$
$C_6F_5AsCH^{+\cdot}$
$C_6F_4AsCH_2^+$
$C_6F_5As^{+\cdot}$
$-AsF$
$C_7F_4H^+$
$-F$
$-HF$
$C_6F_4As^+$
$C_7F_3AsH^+$

greater ability to stabilize positive charge. This facet is also evident in the reaction described below where Route A is preferred for M = N, the ring carrying all the positive charge after cleavage, while Route B is more



important for M = P, As the charge tending to remain with the "softer" heteroatom after cleavage.

An interesting decomposition pathway which is shown in the fragmentation scheme involves a rather drastic rearrangement of the parent ion followed by loss of CH_3MH. Figure 34 shows the possible intermediate species in more detail. The end product of this transition resembles the normal tropyllium-ion which is prevalent in many aromatic spectra. Since this ion represents a pseudo-aromatic system its stability may be the driving force behind such a rearrangement.

As has been observed in many other cases[8-15], loss of MF and MF_2 neutral species to give a variety of fluorocarbon ions is still an important part of the fragmentation process. For both the arsine and phosphine, ions of the form $C_xF_yH_z$ and C_xF_y carry approximately 40% of the total positive ion current. It is still clearly apparent however,

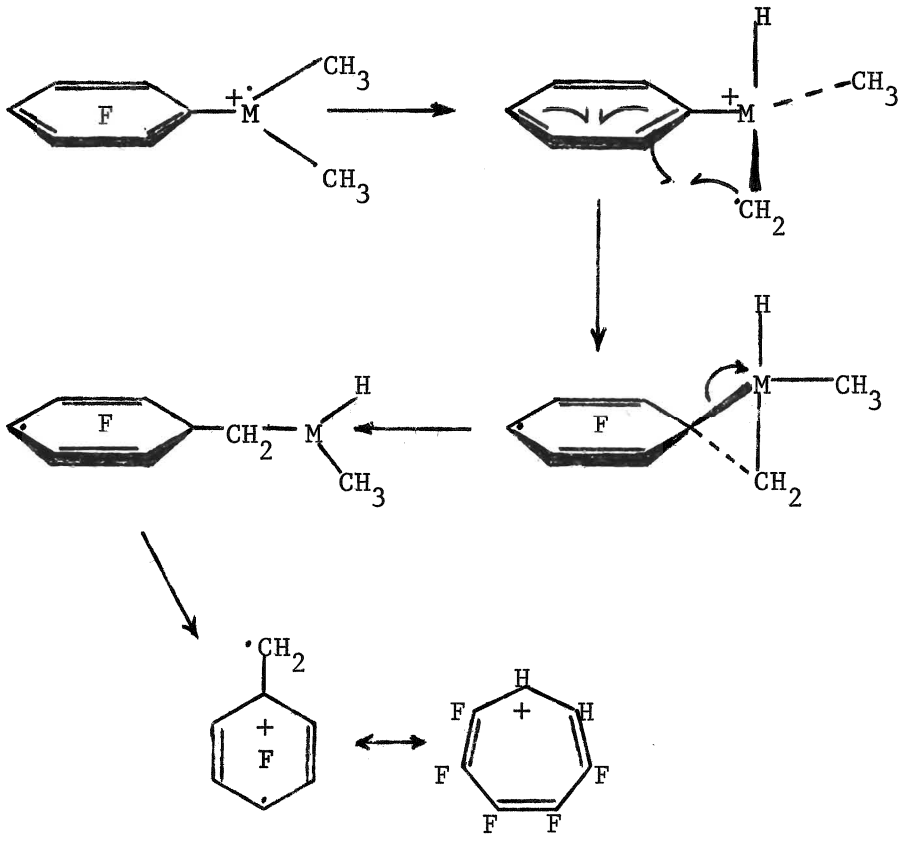


Figure 34

as it was in previous studies by Lanthier and Miller[9] that there is no fluorine transfer to nitrogen thus lending further support to the assumption that vacant heteroatom "p" or "d" orbitals are necessary for such rearrangements to occur.

(b) The Mass Spectra of $(CH_3)_2PX(C_6F_5)$ X = O, S, Se

Table 11 shows the partial mass spectra of these compounds while Fig. 35-37 and 38 display their mass spectra and fragmentation schemes respectively.

The data indicates that X-containing ions are important in the fragmentation of both oxide and sulphide while the selenide derivative behaves much more like the phosphine itself in that loss of an Se radical is the first step in fragmentation. Abundant metastable ions in the spectrum of the oxide revealed several major fragmentation pathways (see Fig. 38a) while the phosphine sulphide and selenide provided only a small amount of metastable support for their breakdown processes.

The relative strengths* of the P=X bond are reflected to some extent in the abundance of the $(M-CH_3)$ species where X = O>S>Se. The pattern continues throughout the spectra as the ions containing the P=X linkage are also subject to the scale of abundance shown above. As was already mentioned, the spectrum of the selenide is low in selenium-containing species, being very similar to the spectrum of the phosphine itself. The phosphine sulphide appears to strike a predictable balance between the oxide and selenide giving rise to a variety of PS containing ions along with species representative of the simple phosphine.

A notable pattern emerging from the phosphine spectrum also holds for these derivatives, namely the detection of a variety of fluorocarbon fragments. The most interesting

---

* $\bar{D}$ $(R_3P=X)$ (kcal/mole)

X =	O	S	Se
	138	91.5	70

See Ref. 80, Vol. 2 & 3

"Text continues on page 85."

PARTIAL MASS SPECTRA OF $(CH_3)_2PX(C_6F_5)$ X = O, S, Se

Ion^+	X = O	X = S	X = Se
$(CH_3)_2PX(C_6F_5)$	9.2	11.1	4.4
$(CH_3)PX(C_6F_5)$	15.7	6.5	0.7
$PX(C_6F_5)$	0.3	1.2	0.2
C_6F_5X	0.1	3.2	0.2
$(CH_3)_2PX$	6.9	5.1	0.4
$(CH_3)PXF$	4.1	1.8	---
PX	6.5	6.6	---
$(CH_3)_2P(C_6F_5)$	0.3	2.3	7.5
$(C_2H_5P(C_6F_5)$	0.2	2.2	4.3
$(CH_3)P(C_6F_5)$	0.5	1.3	3.2
$HCP(C_6F_5)$	0.6	2.8	5.0
$HP(C_6F_5)$	0.2	---	3.2
$(CH_3)_2P$	1.6	3.9	2.4
$(CH_2)_2P$	2.5	2.5	1.8
$C_7F_5H_2$	1.2	4.1	6.8
C_6F_5H	0.2	0.4	0.4
$C_7F_4H_3$	2.4	1.4	1.5
C_7F_4	0.8	---	1.3
C_6F_4	1.5	0.4	0.2
$C_7H_2F_3$	2.1	1.5	2.7
C_6F_3	1.7	0.5	0.3
$C_7H_3F_2$	0.2	0.9	2.1
$C_7H_2F_2$	0.1	0.4	0.4
C_5F_3	1.6	1.6	1.1
C_6F_2H	1.7	1.9	1.8
C_6F_2	0.5	1.1	1.0
C_5F_2H	0.7	1.2	1.4
C_3F_3	0.9	5.1	1.2
C_5HF	0.2	0.5	0.6
C_3F_2H	1.2	1.7	1.2

Figure 35
The Mass Spectrum
of $(C_6F_5)P(O)(CH_3)_2$
at 70 eV

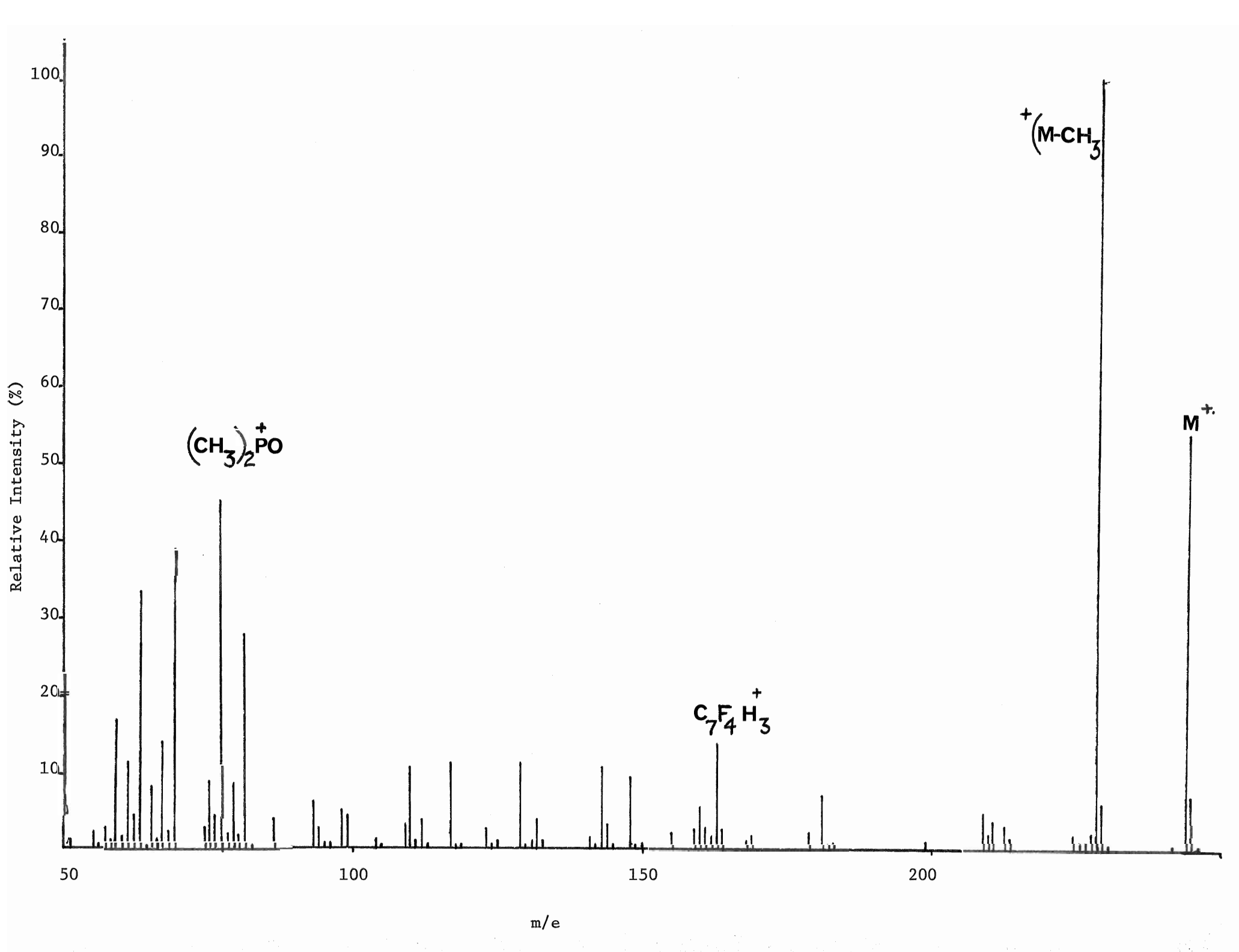

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
m/e
$(CH_3)_2PO^+$
$C_7F_4H_3^+$
$(M-CH_3)^+$
$M^{+\cdot}$

Figure 36
The Mass Spectrum
of $(C_6F_5)P(S)(CH_3)_2$
at 70 eV

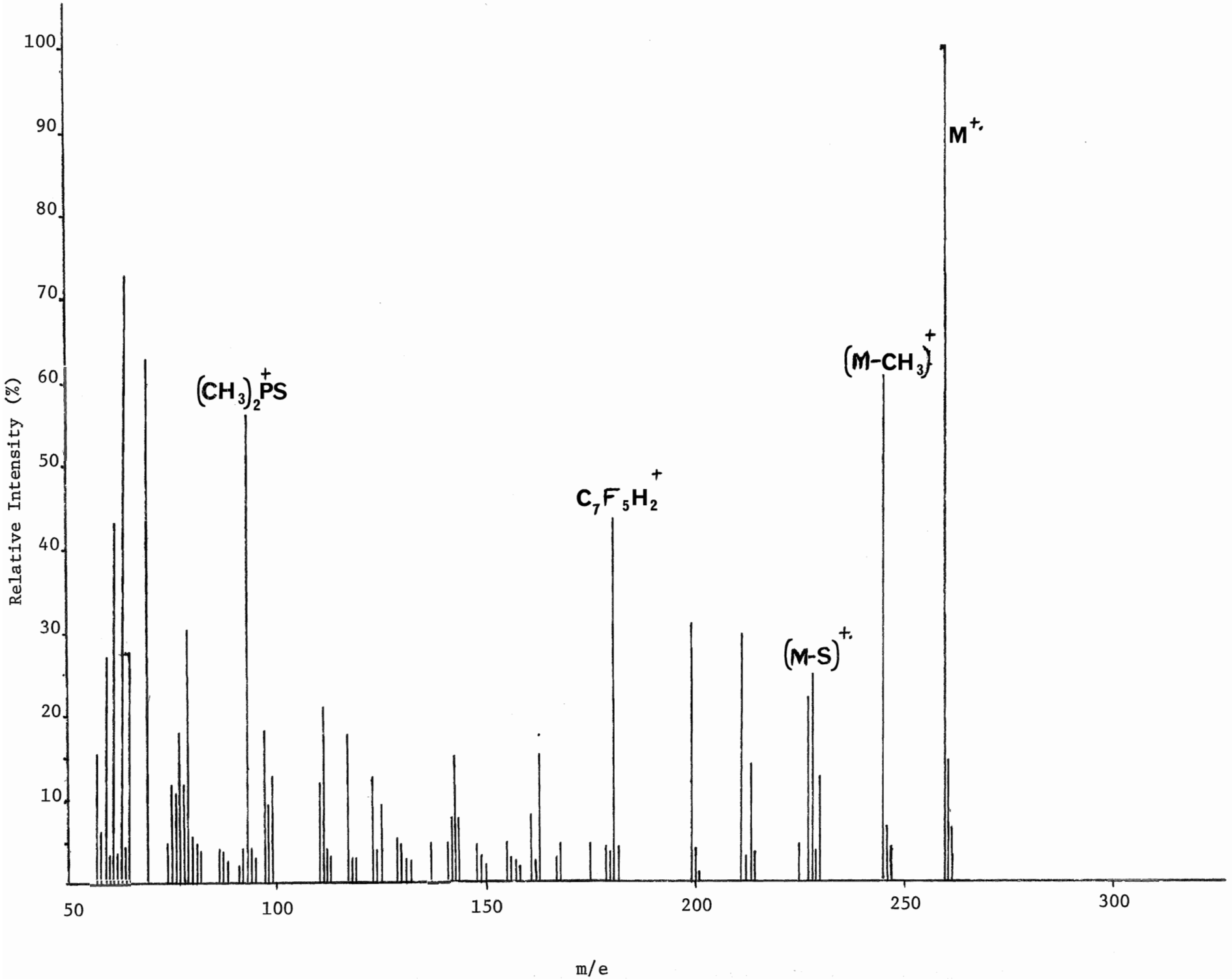

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
$(CH_3)_2PS^+$
$C_7F_5H_2^+$
$(M-CH_3)^+$
$M^{+\cdot}$
$(M-S)^{+\cdot}$
50
100
150
200
250
300
m/e

Figure 37
The Mass Spectrum
of $(C_6F_5)P(Se)(CH_3)_2$
at 70 eV

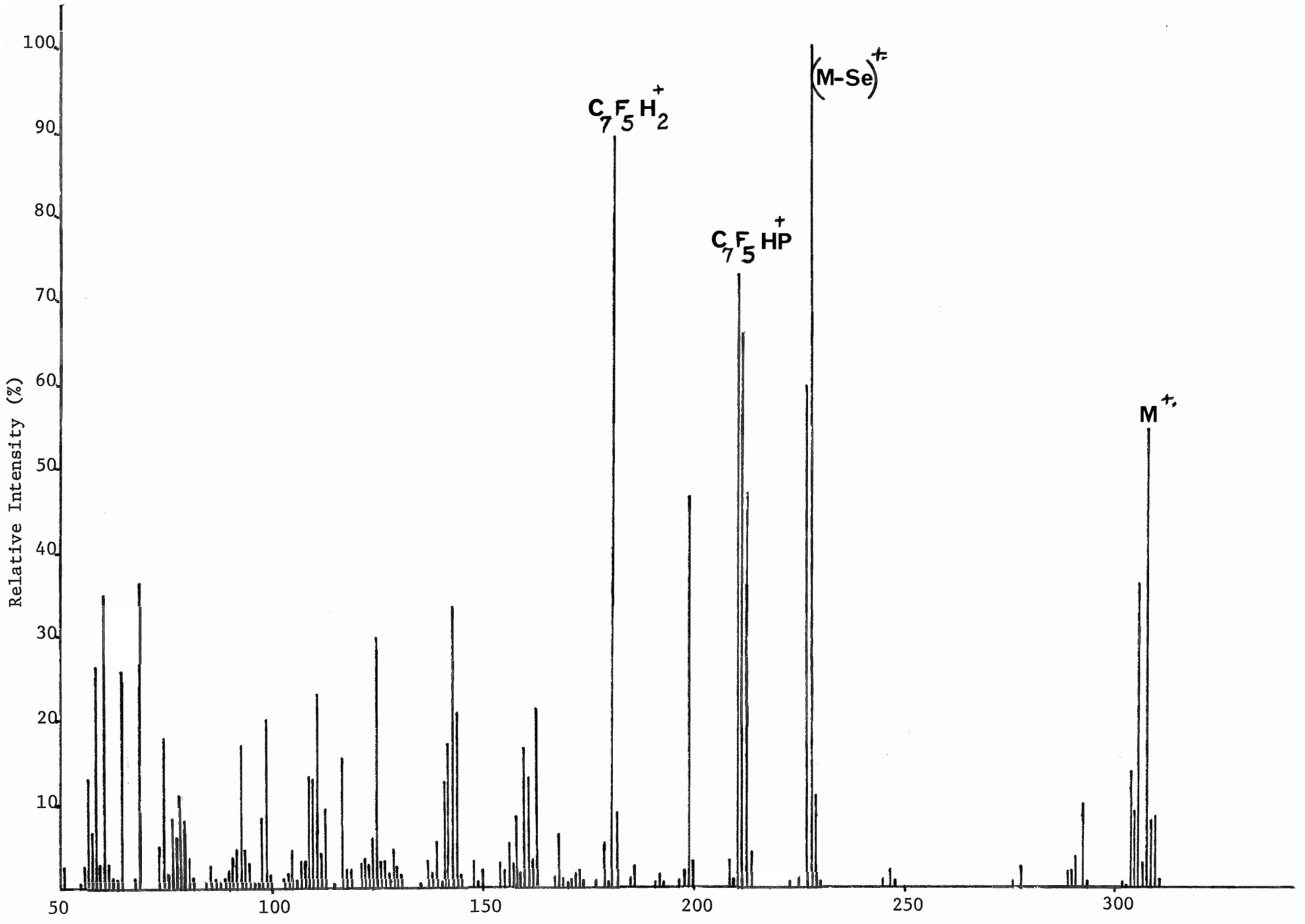
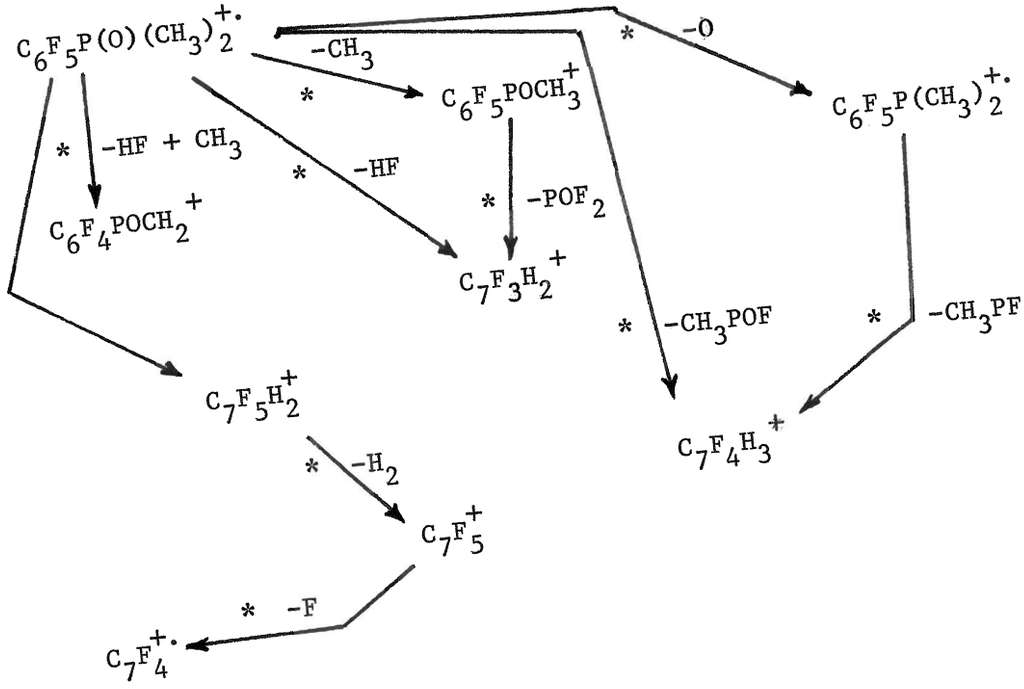

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
$C_7F_5H_2^+$
$C_7F_5HP^+$
$(M-Se)^{+\cdot}$
$M^{+\cdot}$

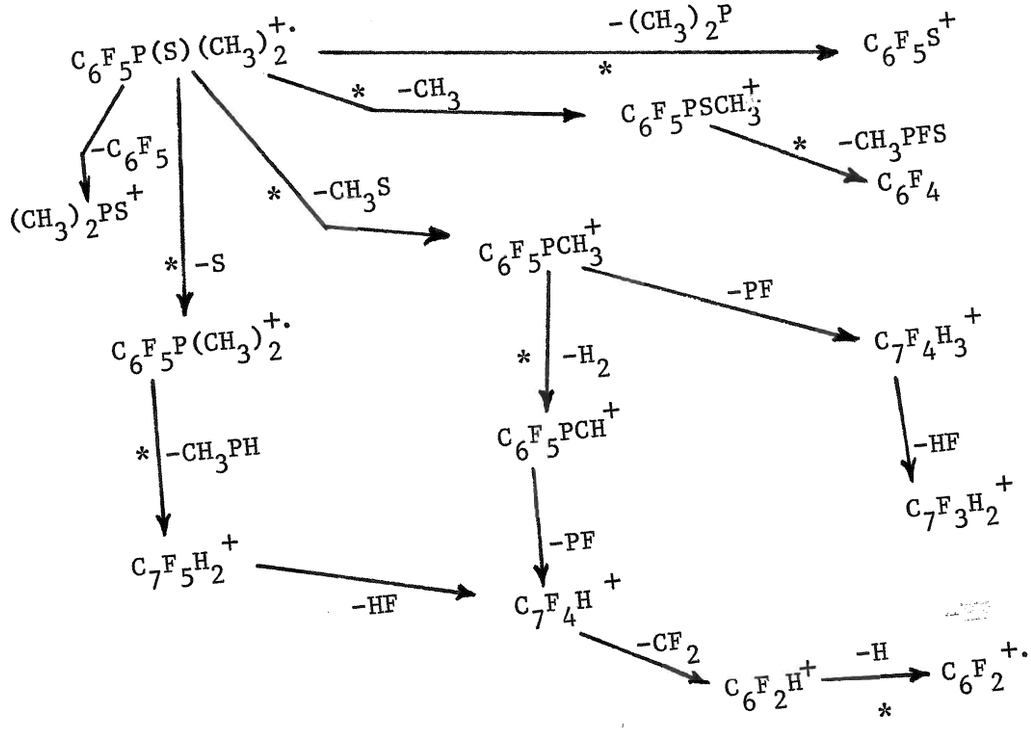
Figure 38
Fragmentation Schemes
for the series $(C_6F_5)P(X)(CH_3)_2$

(A) X = O
(B) X = S
(C) X = Se

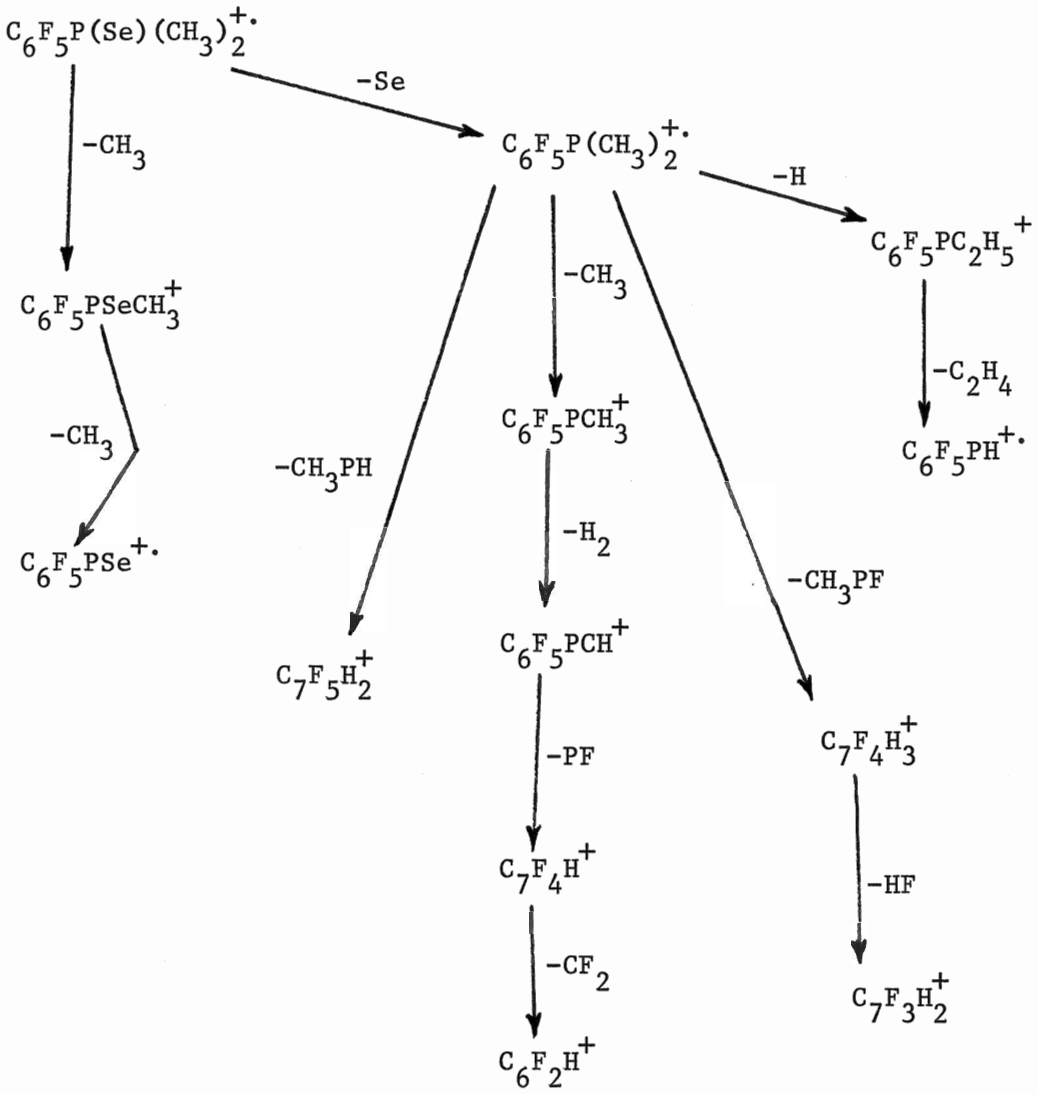
(A)


$C_6F_5P(O)(CH_3)_2^{+\cdot}$
$-CH_3$
$-O$
$C_6F_5POCH_3^+$
$C_6F_5P(CH_3)_2^{+\cdot}$
$-HF + CH_3$
$-HF$
$-POF_2$
$C_6F_4POCH_2^+$
$C_7F_3H_2^+$
$-CH_3POF$
$-CH_3PF$
$C_7F_5H_2^+$
$C_7F_4H_3^+$
$-H_2$
$C_7F_5^+$
$-F$
$C_7F_4^{+\cdot}$

(B)


$C_6F_5P(S)(CH_3)_2^{+\cdot}$
$-(CH_3)_2P$
$C_6F_5S^+$
$-CH_3$
$C_6F_5PSCH_3^+$
$-CH_3PFS$
C_6F_4
$-C_6F_5$
$(CH_3)_2PS^+$
$-CH_3S$
$C_6F_5PCH_3^+$
$-S$
$-PF$
$C_6F_5P(CH_3)_2^{+\cdot}$
$-H_2$
$C_7F_4H_3^+$
$C_6F_5PCH^+$
$-HF$
$-CH_3PH$
$C_7F_3H_2^+$
$-PF$
$C_7F_5H_2^+$
$-HF$
$C_7F_4H^+$
$-CF_2$
$-H$
$C_6F_2H^+$
$C_6F_2^{+\cdot}$

(C)


$C_6F_5P(Se)(CH_3)_2^{+\cdot}$
-Se
$C_6F_5P(CH_3)_2^{+\cdot}$
-CH_3
$C_6F_5PSeCH_3^+$
-CH_3
$C_6F_5PSe^{+\cdot}$
-CH_3PH
$C_7F_5H_2^+$
-CH_3
$C_6F_5PCH_3^+$
-H_2
$C_6F_5PCH^+$
-PF
$C_7F_4H^+$
-CF_2
$C_6F_2H^+$
-H
$C_6F_5PC_2H_5^+$
-C_2H_4
$C_6F_5PH^{+\cdot}$
-CH_3PF
$C_7F_4H_3^+$
-HF
$C_7F_3H_2^+$

of these seem to arise from coupling of the C_6F_5 and methyl substituents giving a variety of tropyllium-like species such as $C_7F_5H_2^+$, $C_7F_4H_3^+$, $C_7F_4^+$, $C_7H_2F_3^+$ and $C_7H_3F_2^+$. Two other significant observations can be made in light of the material described to this point. The first involves formation of P-F bonded fragments such as CH_3PXF, a process which has already been thoroughly described. The second involves rearrangements similar to those observed for the thionophosphonyl and thionophosphinyl halides described earlier. Two cases of this pattern are clearly apparent in the fragmentation of the phosphine sulphide and are depicted below.

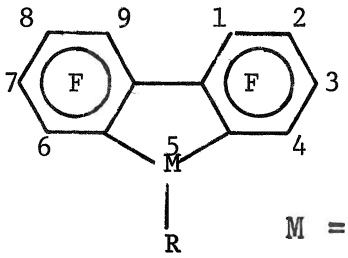
$$(CH_3)_2\overset{+}{P}S(C_6F_5) \longrightarrow (CH_3)\overset{+}{P}C_6F_5 + CH_3S$$

$$(CH_3)_2PS(C_6F_5) \longrightarrow (CH_3)_2P^+ + C_6F_5S$$

(3) Mass Spectra of Some Selected Heterocyclic Systems

(a)* The Mass Spectra of 5-Substituted Octafluorodibenzo Phospholes.

The structure of the compounds described in this section are typified by III. The recent literature[38]



M = P, R = tC_4H_9, C_6H_5, C_6F_5

III

has used this nomenclature to develop some consistency with the growing number of metallole derivatives (M = Group IV element or a transition metal). We will use this description exclusively during this dissertation.

Although the hydrocarbon analogs of III (specifically M = P, R = C_6H_5) have been known since 1953, no comprehensive mass spectral studies have been made until recently. The most important work reported to date, by Hellwinkel et al.[62] describes a number of Group V analogs of III (M = P,As,Sb,Bi; R = CH_3, C_6H_5, 2-$C_{12}H_9$). The phenyl derivatives all exhibited molecular ions, the intensities varying as P>As~Sb»Bi which seems to reflect the expected progression of M-C bond strengths. The 2-biphenylyl deriva-

---

* The mass spectra of the compounds described in this section are shown in Fig. 39-48 with their corresponding fragmentation schemes.

tives exhibit similar behaviour while the methyl-substituted compounds give a large ($M-CH_3$) ion as the base peak in each case. In terms of substitution at phosphorous the general trend in molecular ion abundance is as follows: $C_6H_5 > 2\text{-}C_{12}H_9 > CH_3$. A final interesting aspect of these spectra was the detection of ions corresponding to loss of MH from the $C_{12}H_8MC_6H_5^+$ molecular ion. These fragments, which correspond to $C_{18}H_{13}^+$ are found in 5 - 10% relative abundance and follow the progression Bi~As>Sb>P. Similarly, ions are detected for a number of varied hydrocarbon species of the type $C_{18}H_x$, the other important species being $C_{18}H_{10}$ corresponding to loss of MH_3 from the parent ion. The pathways giving rise to these ions have not been clearly elucidated.

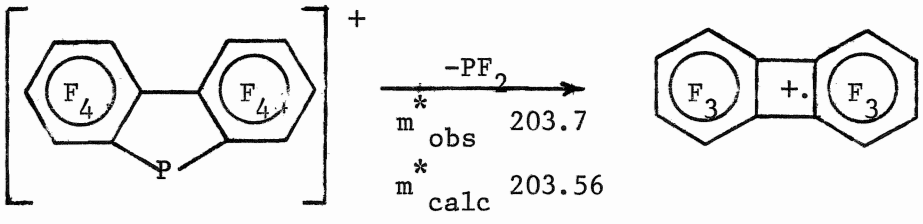
The partial mass spectra of the compounds we have studied are shown in Table 12. The general substitution trend of R reflects a situation similar to that observed by Hellwinkel et al.[62], i.e. the molecular ion abundance follows the pattern $C_6H_5 > C_6F_5 \gg t\text{-}C_4H_9$. Cleavage of the P-R bond is still the major step in fragmentation of the octafluorodibenzophospholes and this process gives rise to a large range in the intensities of the R^+ fragment ions based on their propensity to stabilize a positive charge centre ($C_4H_9 > C_6H_5 > C_6F_5$).

The phenomenon of fluorine transfer rearrangements is also observed in each of the phosphole spectra studied. The most notable example is described in the schematic below.

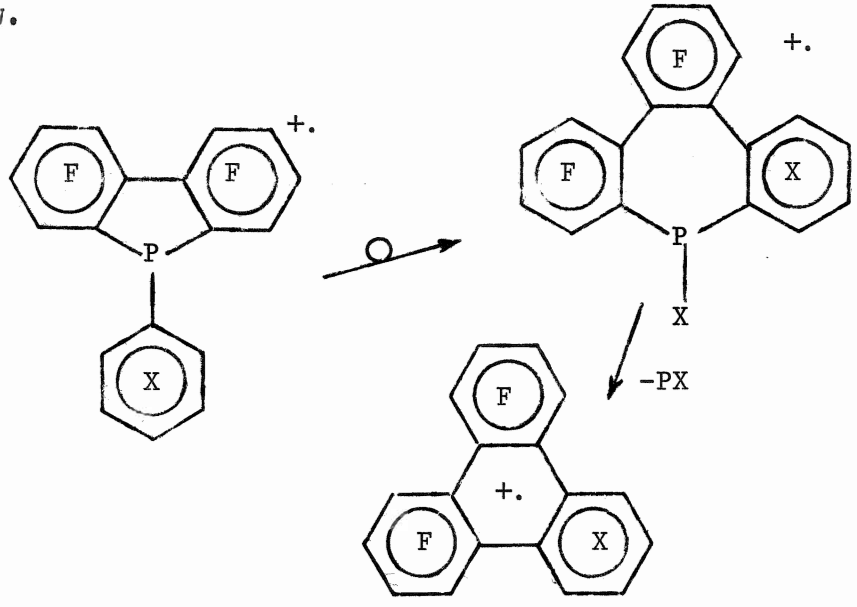
TABLE 12

PARTIAL MASS SPECTRA OF $C_{12}F_8PR$
($C_{12}F_8PR \equiv M$)

Ion$^+$	R =	t-C_4H_9	C_6H_5	C_6F_5
M		0.4	25.8	20.8
M-F		---	2.5	2.9
M-HF		---	0.6	---
M-2F		0.2	0.1	---
M-R		12.1	13.0	33.3
M-R-F		0.1	0.3	0.4
M-R-2F		0.1	---	---
RPF		---	---	0.4
RP		---	---	1.8
R		58.5	20.7	---
$C_{18}F_8X_4$		---	2.4 (X=H)	2.1 (X=F)
$C_{18}F_7X_5$		---	2.3	---
$C_{18}F_7X_4$		---	---	1.6 "
$C_{18}F_6X_4$		---	0.5 "	1.0 "
$C_{12}F_6$		2.9	2.8	8.2
$C_{12}F_5$		0.3	0.4	1.5
$C_{11}F_5$		0.3	0.3	1.7
C_6F_3		---	---	0.6
C_5F_3		---	---	0.5



where R = C_6H_5 and C_6F_5, a variety of poly fluoroaromatic species are detected in the mass spectra. These can be rationalized in terms of PX_n (n = 1,2,3; X = F or H) losses from the parent ion via the type of intermediate shown below.



Such species have been postulated in previous studies involving phosphorous[10] and Group IV compounds[14].

The delocalization of the non-bonding electron pair on phosphorous has been the topic of much discussion for phosphole systems[43,48,67] and theoretical treatments[62] support these conjugation effects. A strong molecular ion was cited as evidence for aromatic character in 1-

"Text continues on page 94"

Figure 39
The Mass Spectrum
of $(C_{12}F_8)P(t\text{-}C_4H_9)$
at 70 eV

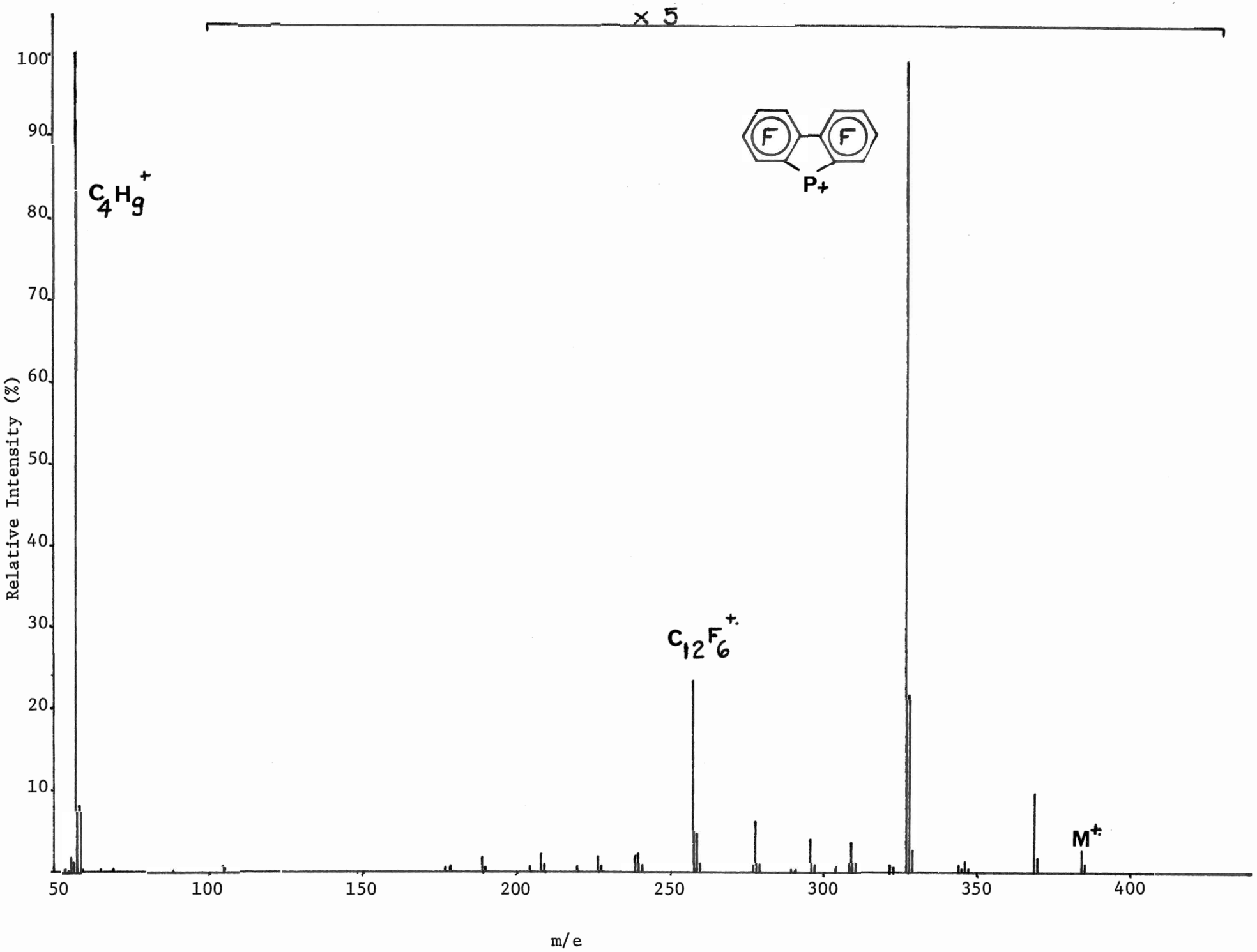

× 5
100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
$C_4H_9^+$
F
F
P+
$C_{12}F_6^{+\cdot}$
$M^{+\cdot}$
50
100
150
200
250
300
350
400
m/e

Figure 40
The Mass Spectrum
of $(C_{12}F_8)P(C_6H_5)$
at 70 eV

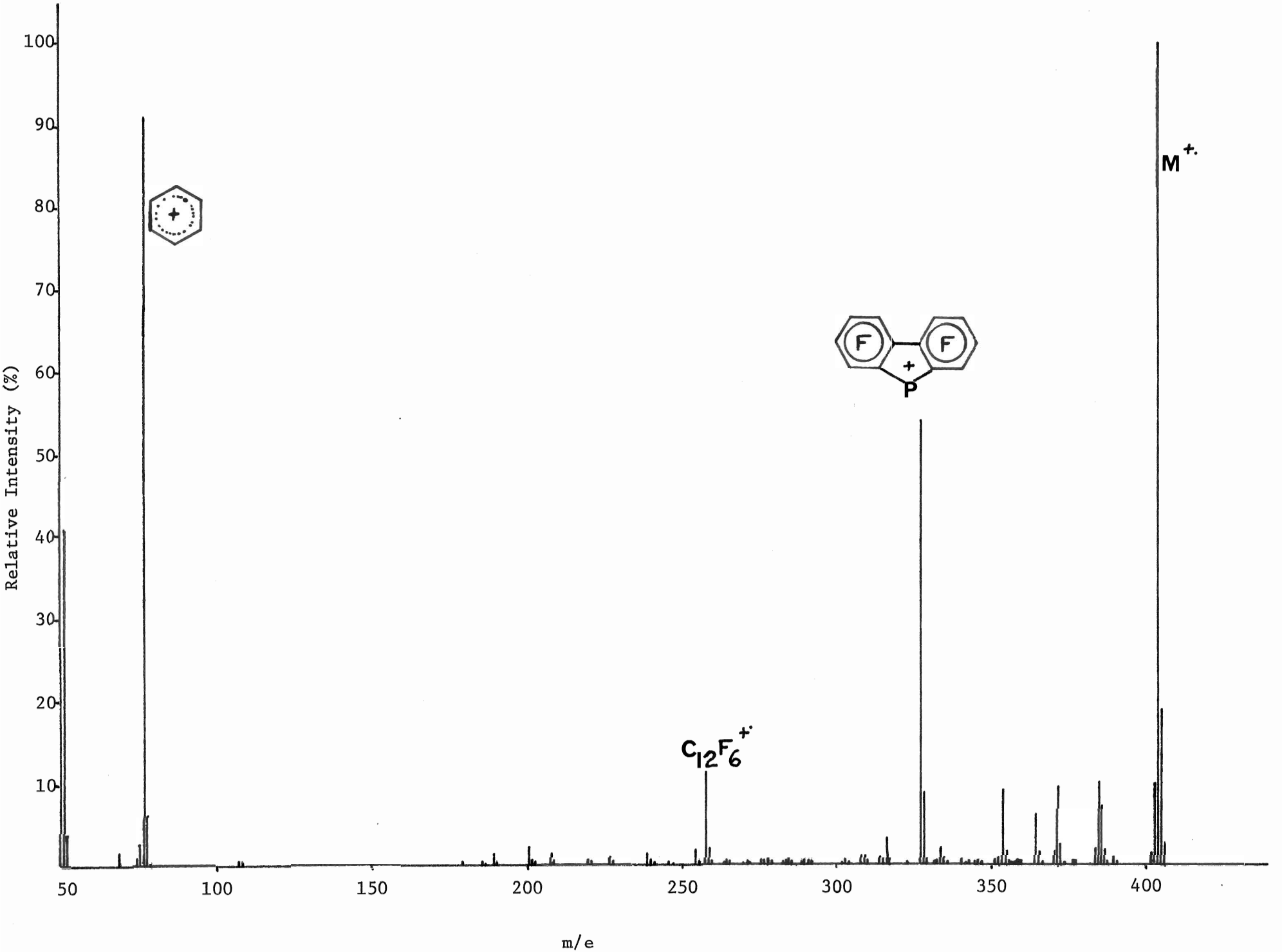

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
m/e
M+.
C12F6+.
F
F
+
P

Figure 41
The Mass Spectrum
of $(C_{12}F_8)P(C_6F_5)$
at 70 eV

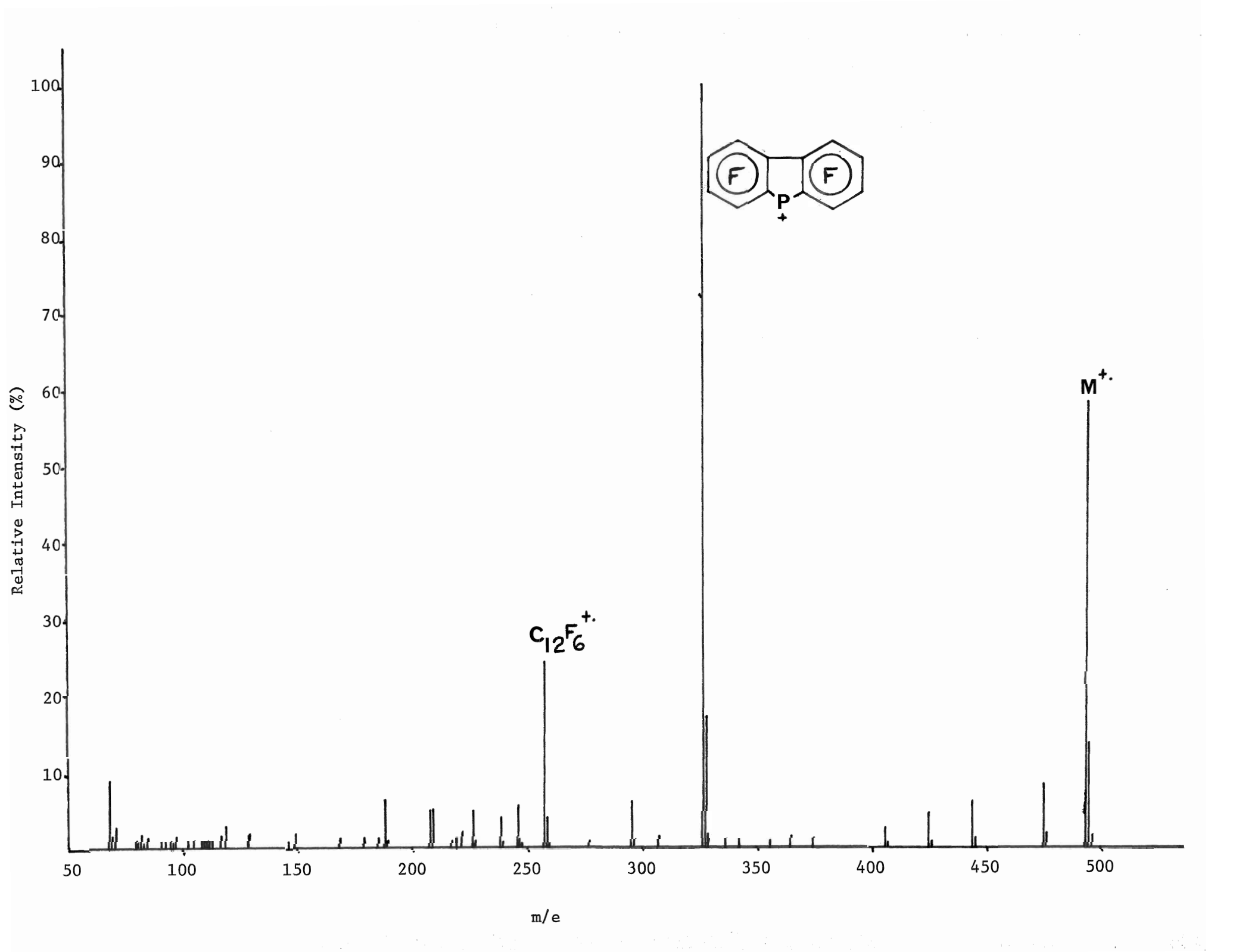
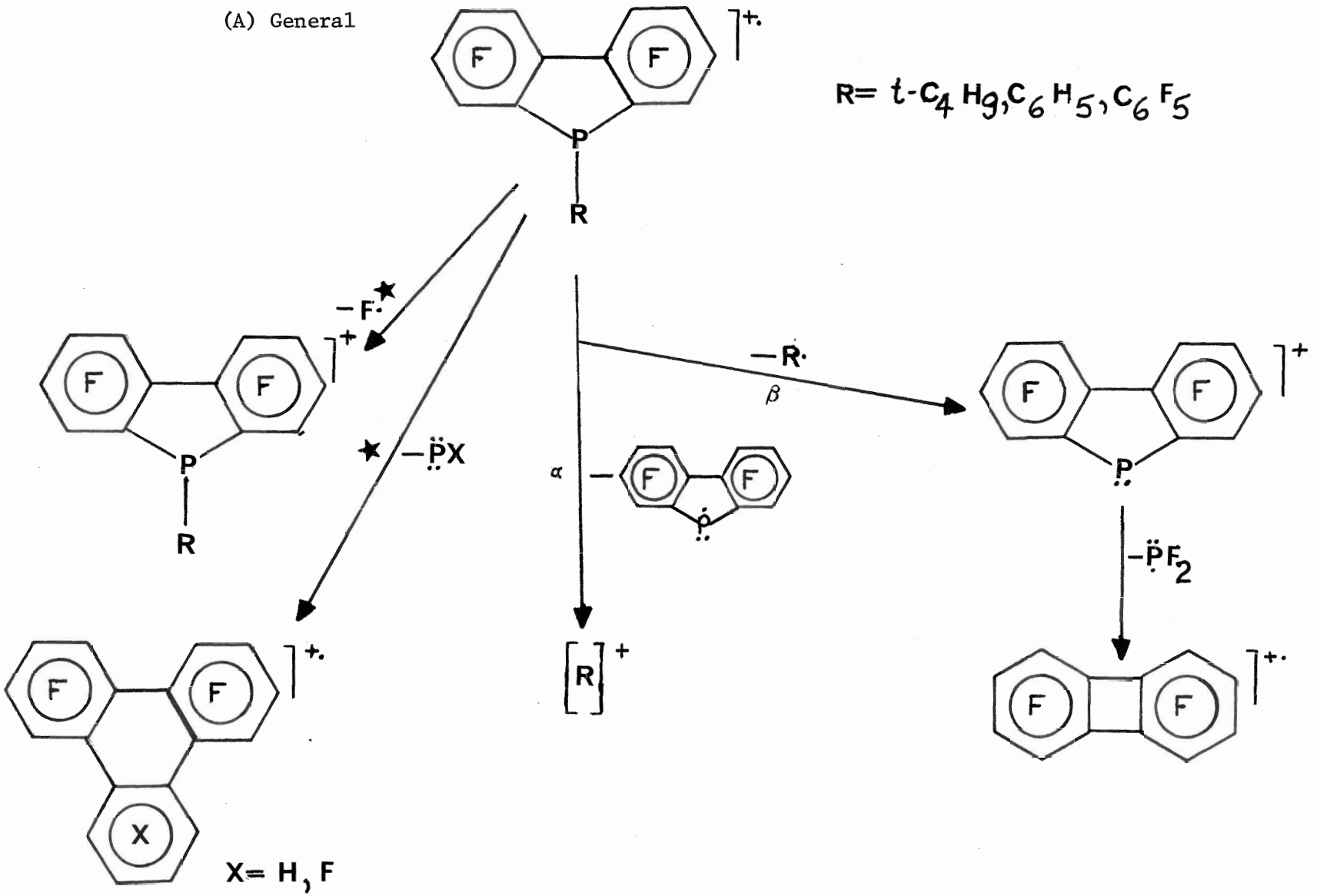

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
450
500
m/e
F
F
P
+
M+.
C12F6+.

Figure 42
Fragmentation Schemes
for the series $(C_{12}F_8)PR$

(A) General
(B) R = t-C_4H_9
(C) R = C_6H_5
(D) R = C_6F_5

(A) General

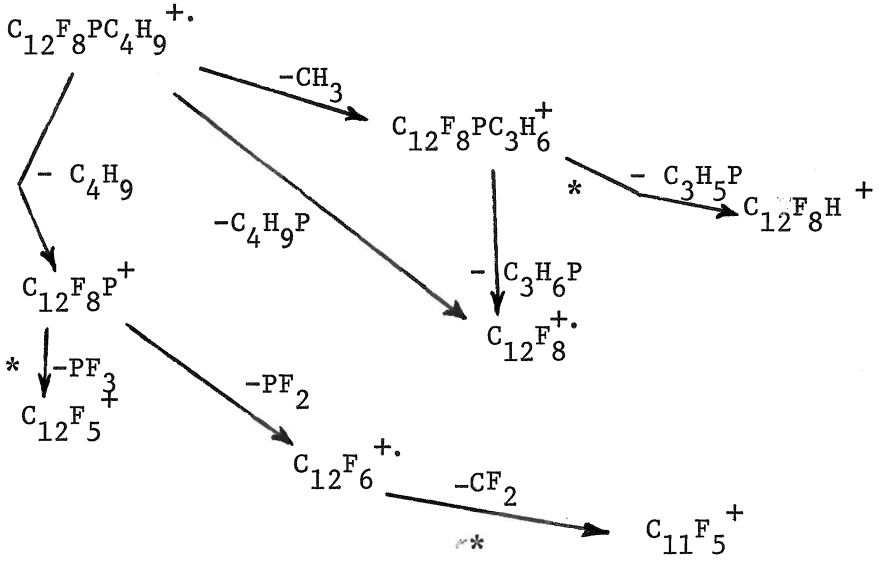


★ NOT OBSERVED FOR R=C_4H_9

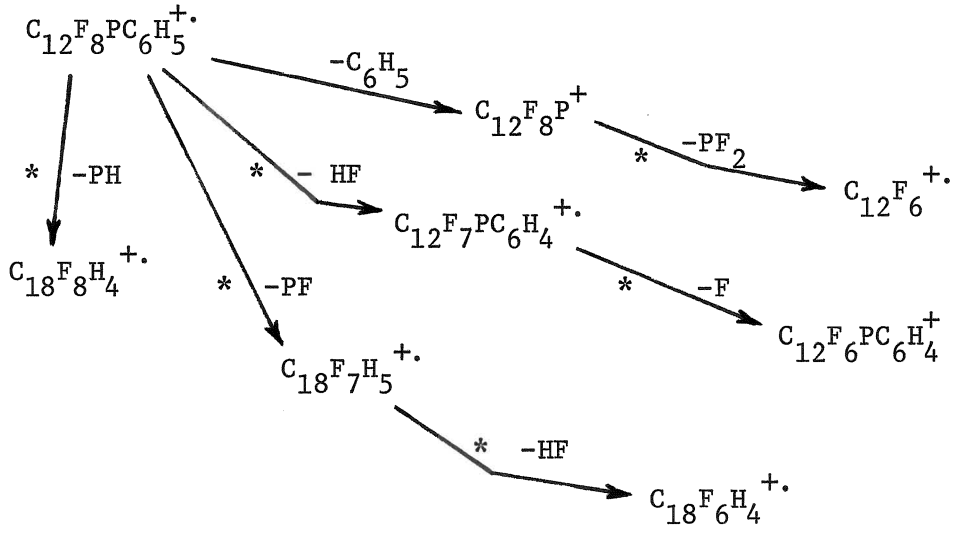
α PREDOMINANT FOR R=C_4H_9, C_6H_5

β " " R=C_6F_5

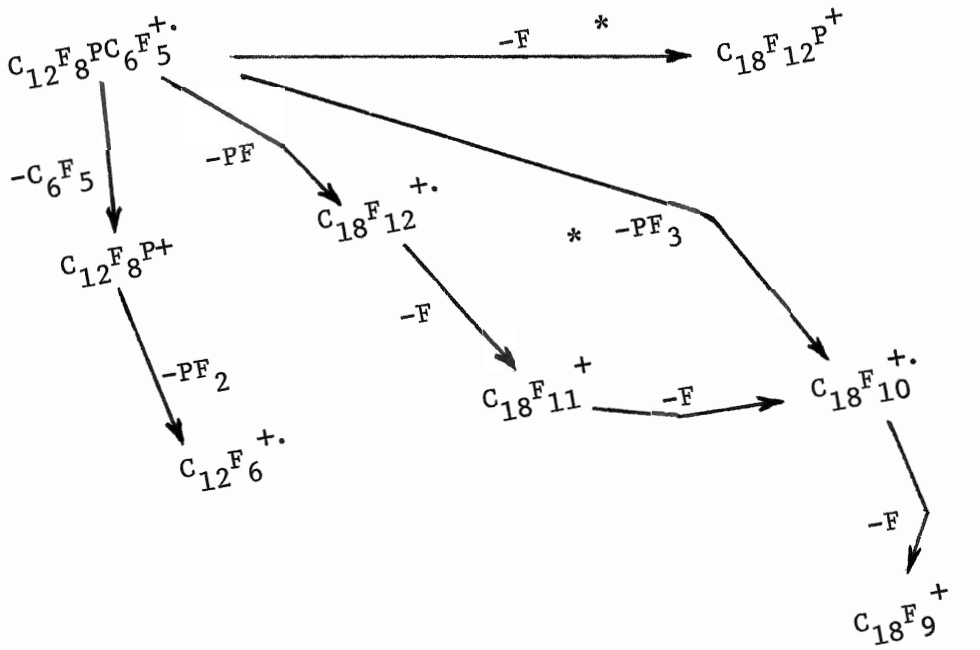
(B)


$C_{12}F_8PC_4H_9^{+\cdot}$
$-CH_3$
$C_{12}F_8PC_3H_6^+$
$-C_4H_9$
$-C_4H_9P$
$*\ -C_3H_5P$
$C_{12}F_8H^+$
$-C_3H_6P$
$C_{12}F_8^{+\cdot}$
$C_{12}F_8P^+$
$*\ -PF_3$
$C_{12}F_5^+$
$-PF_2$
$C_{12}F_6^{+\cdot}$
$-CF_2$
$C_{11}F_5^+$

(C)


$C_{12}F_8PC_6H_5^{+\cdot}$
$-C_6H_5$
$C_{12}F_8P^+$
$*\ -PH$
$C_{18}F_8H_4^{+\cdot}$
$*\ -HF$
$C_{12}F_7PC_6H_4^{+\cdot}$
$*\ -PF_2$
$C_{12}F_6^{+\cdot}$
$*\ -PF$
$C_{18}F_7H_5^{+\cdot}$
$*\ -F$
$C_{12}F_6PC_6H_4^+$
$*\ -HF$
$C_{18}F_6H_4^{+\cdot}$

(D)


$C_{12}F_8PC_6F_5^{+\cdot}$
-F
*
$C_{18}F_{12}P^+$
$-C_6F_5$
-PF
$C_{18}F_{12}^{+\cdot}$
$C_{12}F_8P^+$
* $-PF_3$
-F
$-PF_2$
$C_{18}F_{11}^+$
-F
$C_{18}F_{10}^{+\cdot}$
$C_{12}F_6^{+\cdot}$
-F
$C_{18}F_9^+$

methyl phosphole[48] when a comparison of its mass spectrum was made with the related compounds furan, thiophene, pyrrole and N-methyl pyrrole.

On this basis it may be useful to compare the pertinent phospholes under discussion with their corresponding open systems, namely $(C_6F_5)_3P$ and $C_{12}F_8PC_6F_5$ or $(C_6F_5)_2PC_6H_5$ and $C_{12}F_8PC_6H_5$. The values of their net abundance are shown in the table below.

TABLE 13

Ion^+	Abundance (% of total + ve Ionization)
$(C_6F_5)_3P$	42.0[a]
$(C_6F_5)_2P(C_6H_5)$	15.7[a]
$(C_{12}F_8)PC_6F_5$	20.8
$(C_{12}F_8)PC_6H_5$	25.8

a values taken from reference (14)

The results of such a comparison are obviously ambiguous though the phenyl derivatives seem to indicate an increase in stability for the heterocyclic system.

(b) Heterocyclic Transition Metal Compounds: The Mass Spectra of Metalloles.

These compounds have structures similar to that given as III in section (a) with the general formulae $C_{12}F_8MRR'$. The specific compounds presented in this study are M = Co, Rh, Ir; R = C_5H_5, R' = CO and M = Ti;

R = R' = $\pi - C_5H_5$. The partial mass spectra of these derivatives are shown in Table 14 as a percentage of the total ion current summed over all isotopic contributions.

The titanium derivative was the first example of a compound of this type and was originally reported by Cohen and Massey[36]. Subsequently, Rausch and co-workers have prepared several examples of titanium[69], hafnium[70], cobalt, rhodium, iridium, platinum and zirconium[22] heterocycles. As yet, no mass spectral studies of these compounds have been undertaken other than for simple molecular weight determinations. The mass spectra of these species with their related fragmentation schemes are presented in Figs. 43 - 48.

(i) $C_{12}F_8M(\pi-C_5H_5)CO$ M = Co, Rh, IR

The basic fragmentation route for these compounds is fairly obvious involving cleavage of the metallole" ring structure after initial loss of carbonyl. This gives rise to the $(C_5H_5)M$ ion as the base peak for M = Co and Rh. For iridium, a much smaller contribution by this ion is evident, the base peak being the ion arising from loss of carbonyl. Indeed, as one proceeds down the group of metals, the intensity of the M-CO) ion increases rapidly, i.e. Co<Rh<Ir. This behaviour is probably due to an increasing propensity for the metal atom to stabilize the positive charge rather than any special stability gained by delocalization of the charge over the aromatic system.

"Text continues on page 103."

TABLE 14

PARTIAL MASS SPECTRA OF $C_{12}F_8M(\pi\text{-}C_5H_5)R$

Ion$^+$	M = Co, R = CO	Rh, CO	Ir, CO	Ti, (π-C_5H_5)
$C_{12}F_8M(C_5H_5)R$	6.5	3.9	7.9	4.5
$C_{12}F_8M(C_5H_5)$	4.0	13.4	28.2	0.4
$C_{12}F_8M(C_5H_5)^{++}$	0.6	0.6	6.0	---
$C_{12}F_8M$	---	---	1.5	---
$C_{12}F_7M(C_5H_5)$	0.2	0.2	---	---
$C_{12}F_7M(C_5H_4)R$	0.3	---	---	13.5
$C_{12}F_7M(C_5H_4)$	1.5	0.4	---	---
$C_{12}F_6M(C_5H_3)$	1.5	0.3	3.3	---
$C_{12}F_5M(C_5H_2)$	0.7	---	1.6	---
$C_5H_5MF_2$	---	---	---	4.2
C_5H_5MF	---	---	---	23.1
C_5H_5M	33.6	40.3	2.0	2.1
C_3H_3M	2.2	3.5	1.1	---
MF_2	---	---	---	3.4
MF	---	---	---	1.1
M	4.5	4.0	---	---
$C_{12}F_7C_5H_4$	1.2	0.4	0.4	---
$C_{12}F_6C_5H_4$	0.6	0.2	---	---
$C_{12}F_6C_5H_3$	0.5	0.2	---	---
$C_{12}F_5C_5H_4$	1.9	0.2	---	---
$C_{12}F_8H_2$	3.7	1.6	1.9	0.4
$C_{12}F_8H$	0.4	0.2	---	0.4
$C_{12}F_8$	0.7	0.3	---	---
$C_{12}F_6$	1.0	---	---	0.3
CF_3	2.4	1.8	5.9	1.0
C_5H_5	1.7	0.6	1.1	1.2

Figure 43
The Mass Spectrum
of $(C_{12}F_8)Co(\pi\text{-}C_5H_5)CO$
at 70 eV

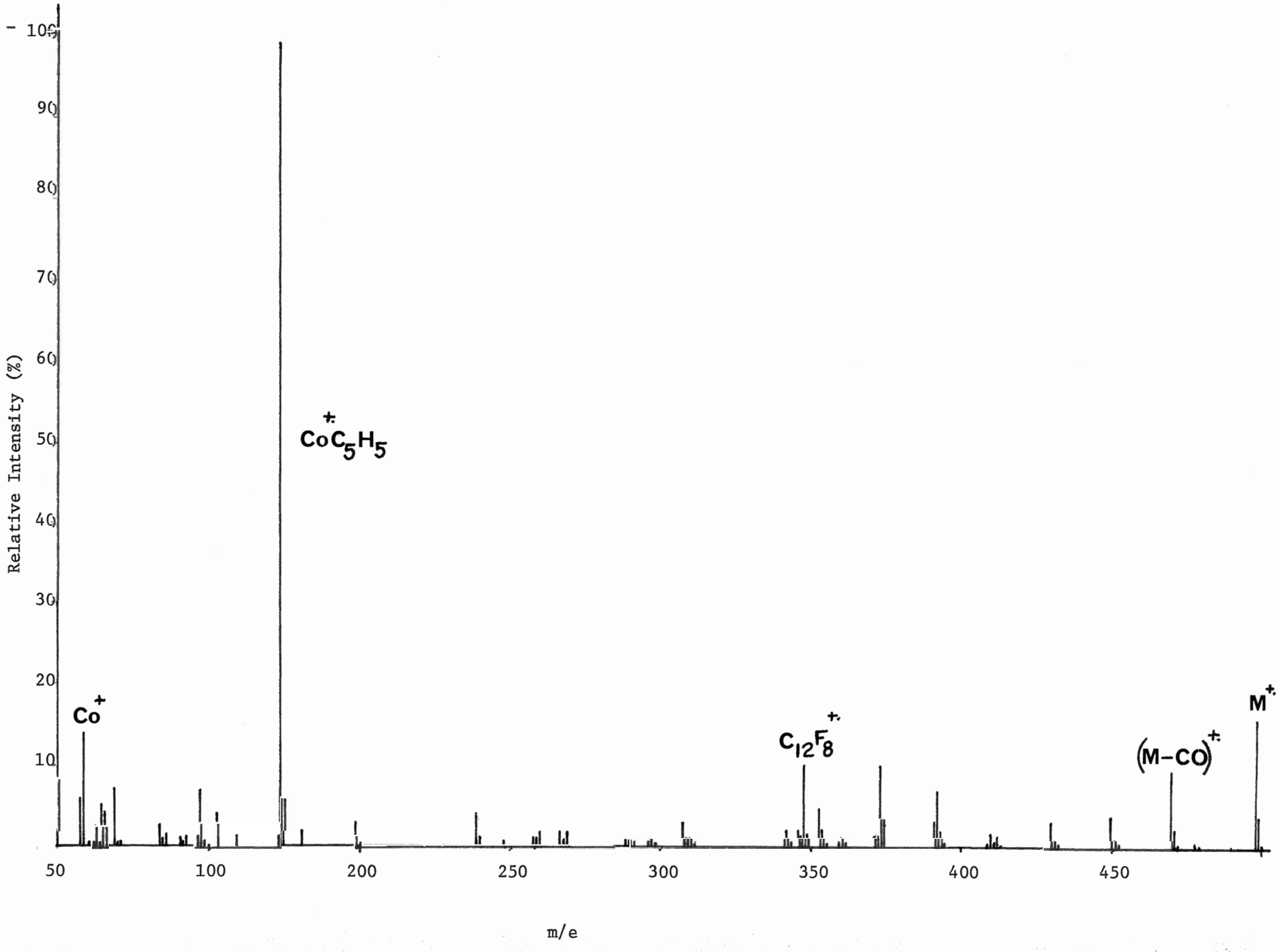

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
Co^+
$CoC_5H_5^{+\cdot}$
$C_{12}F_8^{+\cdot}$
$(M-CO)^{+\cdot}$
$M^{+\cdot}$
50
100
200
250
300
350
400
450
m/e

Figure 44
The Mass Spectrum
of $(C_{12}F_8)Rh(\pi\text{-}C_5H_5)CO$
at 70 eV

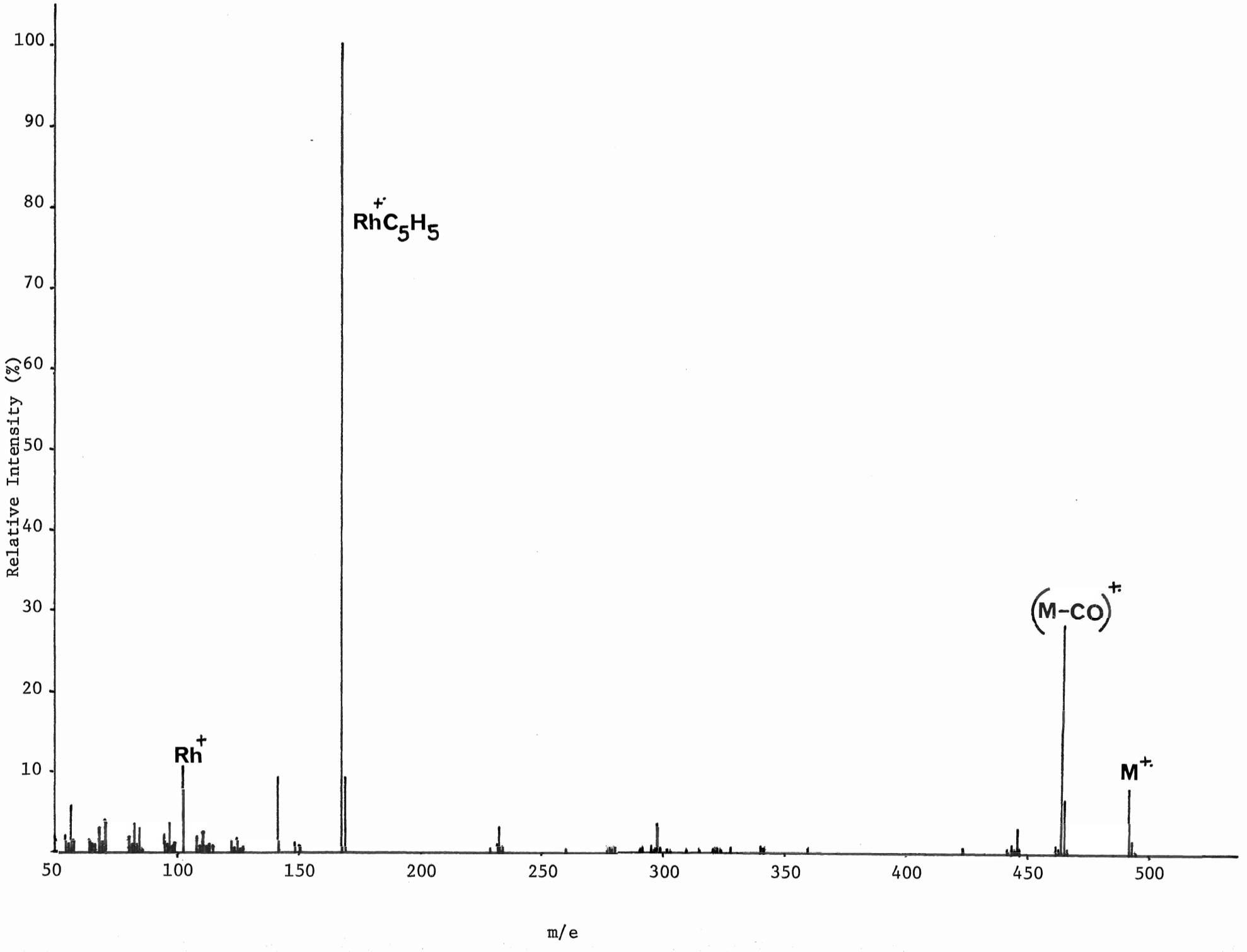

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
$RhC_5H_5^{+\cdot}$
Rh^+
$(M-CO)^{+\cdot}$
$M^{+\cdot}$
50
100
150
200
250
300
350
400
450
500
m/e

Figure 45
The Mass Spectrum
of $(C_{12}F_8)Ir(\pi\text{-}C_5H_5)CO$
at 70 eV

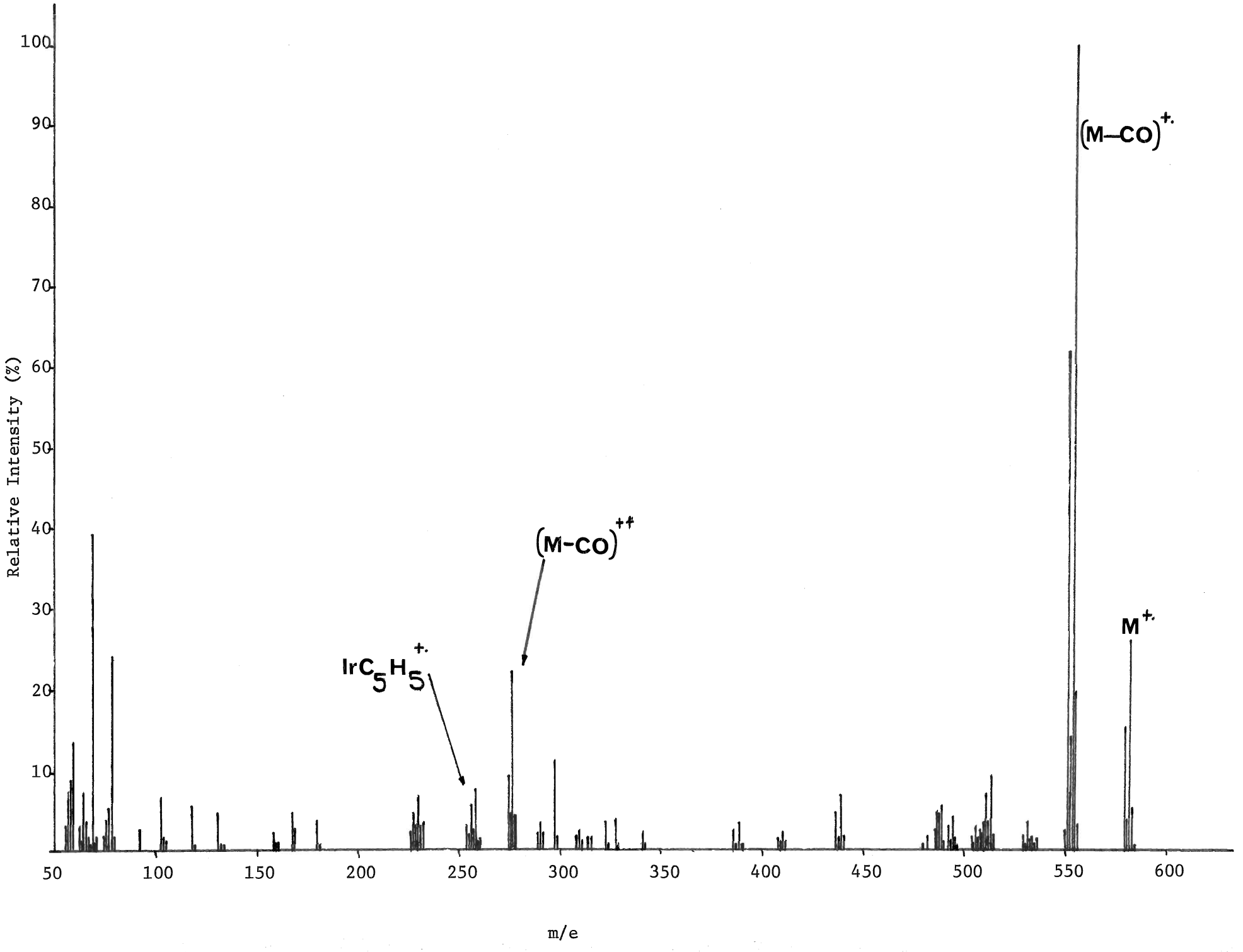
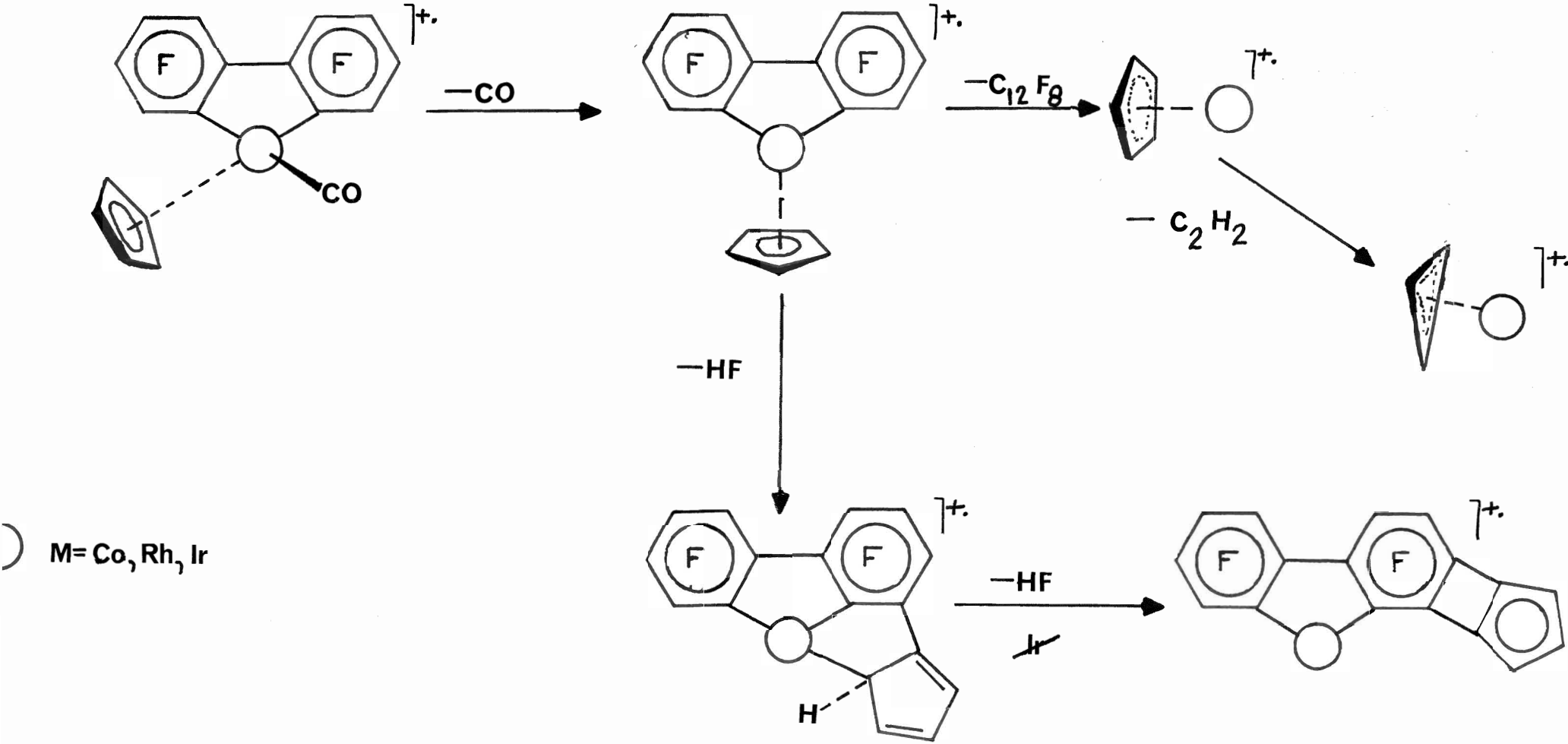

100
90
80
70
60
50
40
30
20
10
Relative Intensity (%)
50
100
150
200
250
300
350
400
450
500
550
600
m/e
(M–CO)+.
(M-CO)++
IrC5H5+.
M+.

Figure 46
Fragmentation Schemes
for the series $(C_{12}F_8)M(\pi\text{-}C_5H_5)CO$

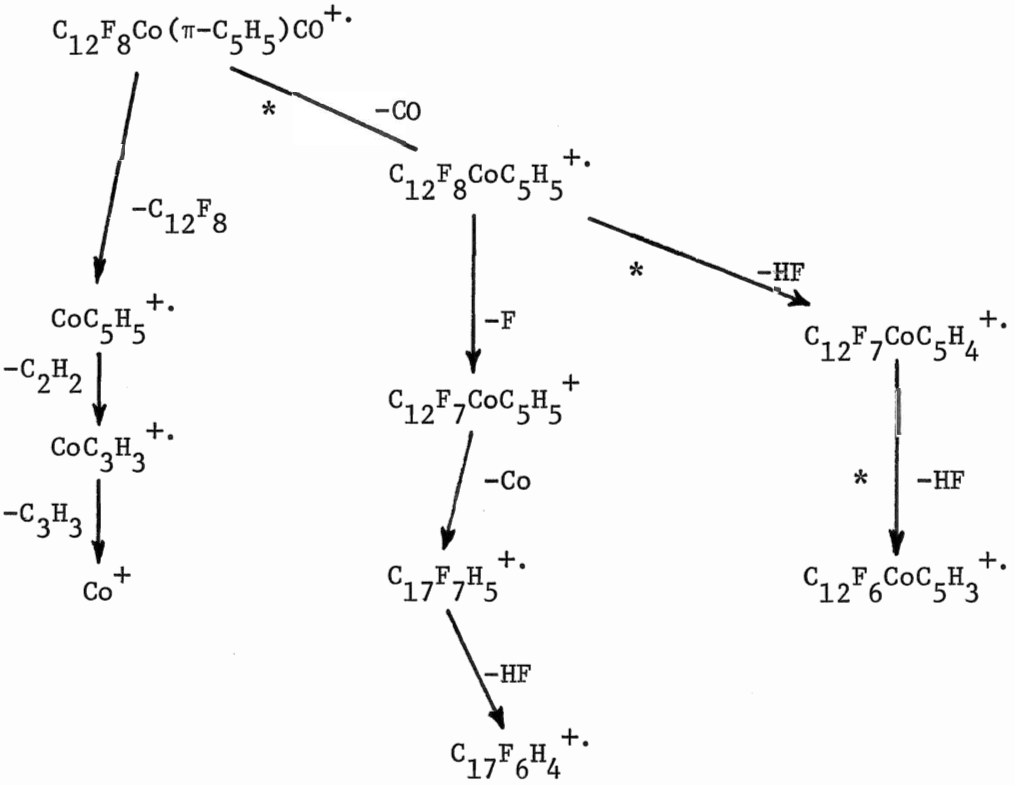
(A) General
(B) M = Co
(C) M = Rh
(D) M = Ir

(A) General

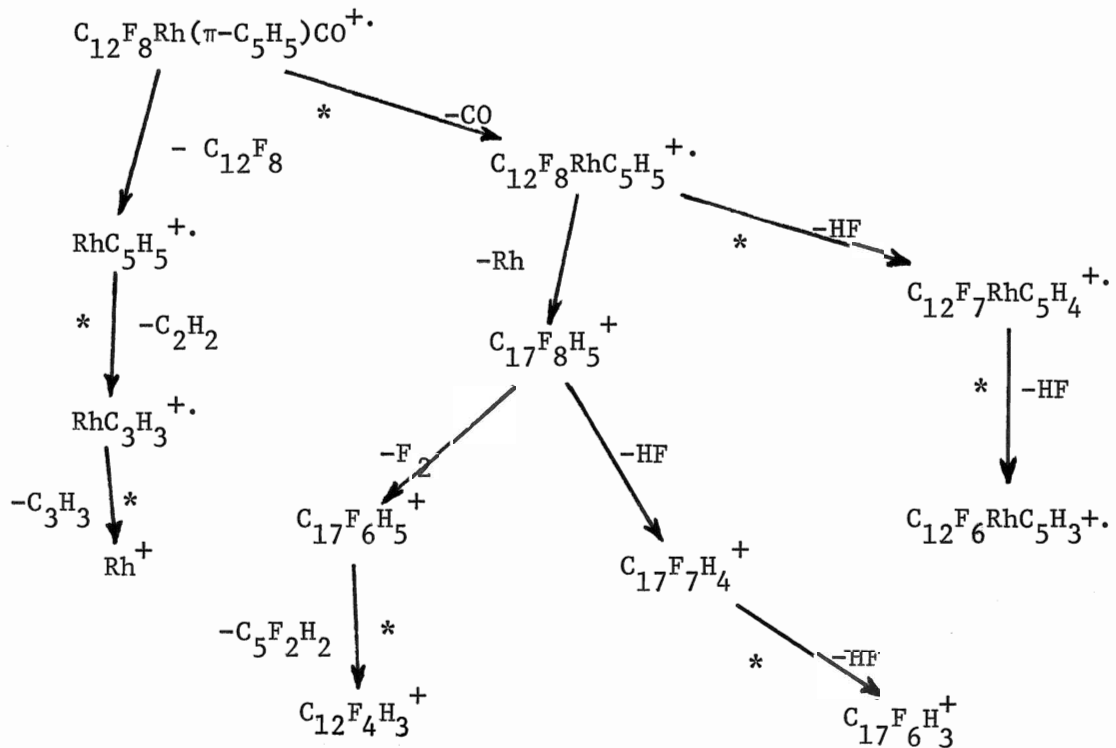


M= Co, Rh, Ir

(B)


$C_{12}F_8Co(\pi\text{-}C_5H_5)CO^{+\cdot}$
*
-CO
$C_{12}F_8CoC_5H_5^{+\cdot}$
$-C_{12}F_8$
$CoC_5H_5^{+\cdot}$
$-C_2H_2$
$CoC_3H_3^{+\cdot}$
$-C_3H_3$
Co^+
-F
$C_{12}F_7CoC_5H_5^+$
-Co
$C_{17}F_7H_5^{+\cdot}$
-HF
$C_{17}F_6H_4^{+\cdot}$
*
-HF
$C_{12}F_7CoC_5H_4^{+\cdot}$
*
-HF
$C_{12}F_6CoC_5H_3^{+\cdot}$

(C)


$C_{12}F_8Rh(\pi\text{-}C_5H_5)CO^{+\cdot}$
*
-CO
$C_{12}F_8RhC_5H_5^{+\cdot}$
$-C_{12}F_8$
$RhC_5H_5^{+\cdot}$
*
$-C_2H_2$
$RhC_3H_3^{+\cdot}$
$-C_3H_3$
*
Rh^+
-Rh
$C_{17}F_8H_5^+$
$-F_2$
$C_{17}F_6H_5^+$
$-C_5F_2H_2$
*
$C_{12}F_4H_3^+$
-HF
$C_{17}F_7H_4^+$
*
-HF
$C_{17}F_6H_3^+$
*
-HF
$C_{12}F_7RhC_5H_4^{+\cdot}$
*
-HF
$C_{12}F_6RhC_5H_3^{+\cdot}$

(D)

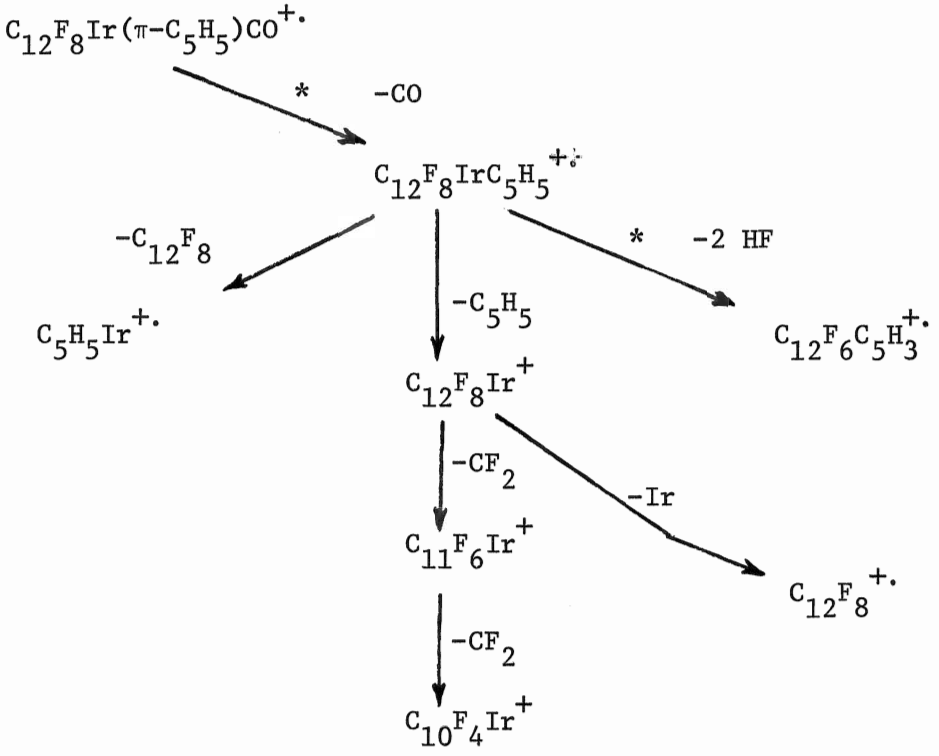

$C_{12}F_8Ir(\pi\text{-}C_5H_5)CO^{+\cdot}$
*
-CO
$C_{12}F_8IrC_5H_5^{+\cdot}$
$-C_{12}F_8$
$C_5H_5Ir^{+\cdot}$
$-C_5H_5$
*
-2 HF
$C_{12}F_6C_5H_3^{+\cdot}$
$C_{12}F_8Ir^+$
$-CF_2$
$C_{11}F_6Ir^+$
-Ir
$C_{12}F_8^{+\cdot}$
$-CF_2$
$C_{10}F_4Ir^+$

Figure 47
The Mass Spectrum
of $(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2$
at 70 eV

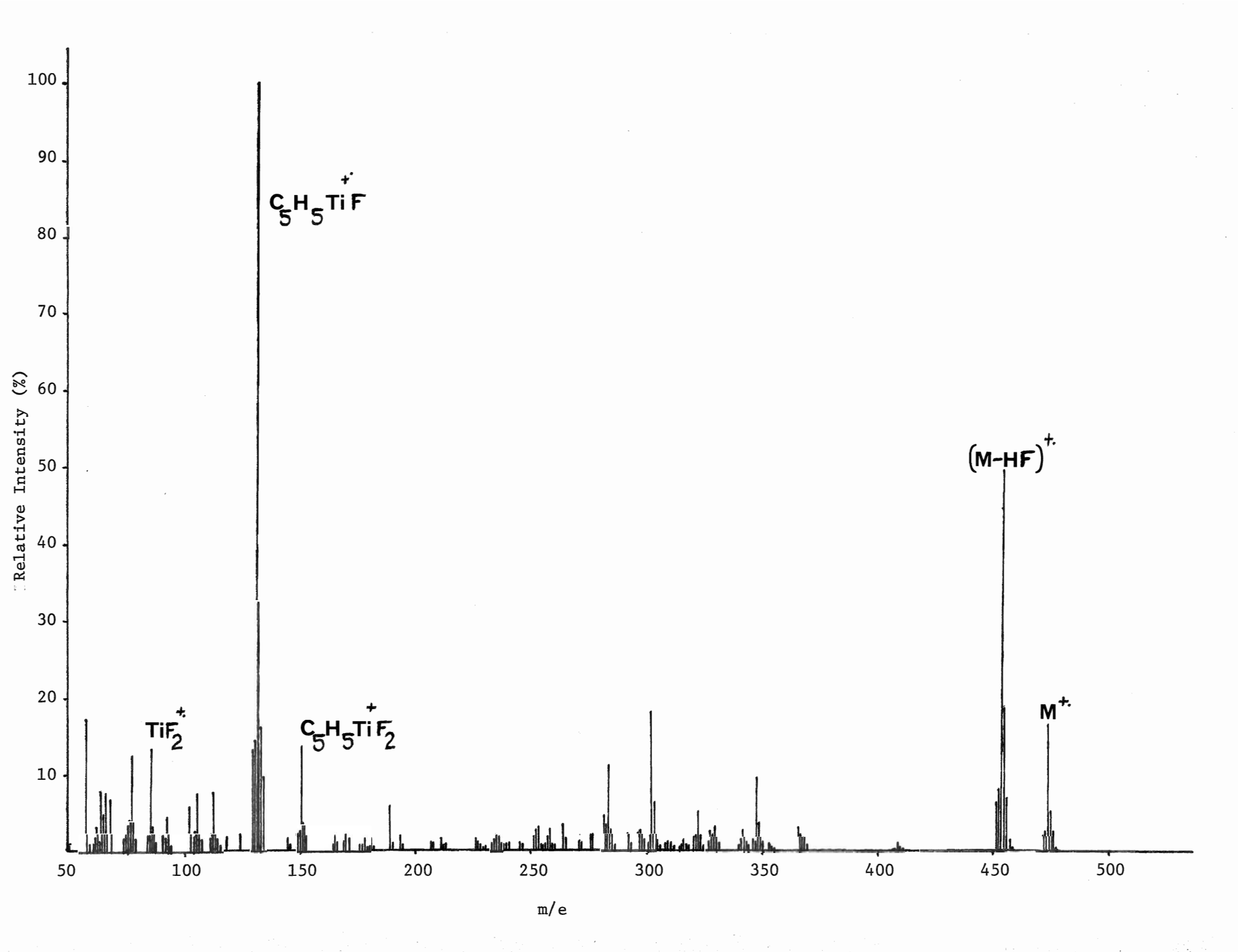
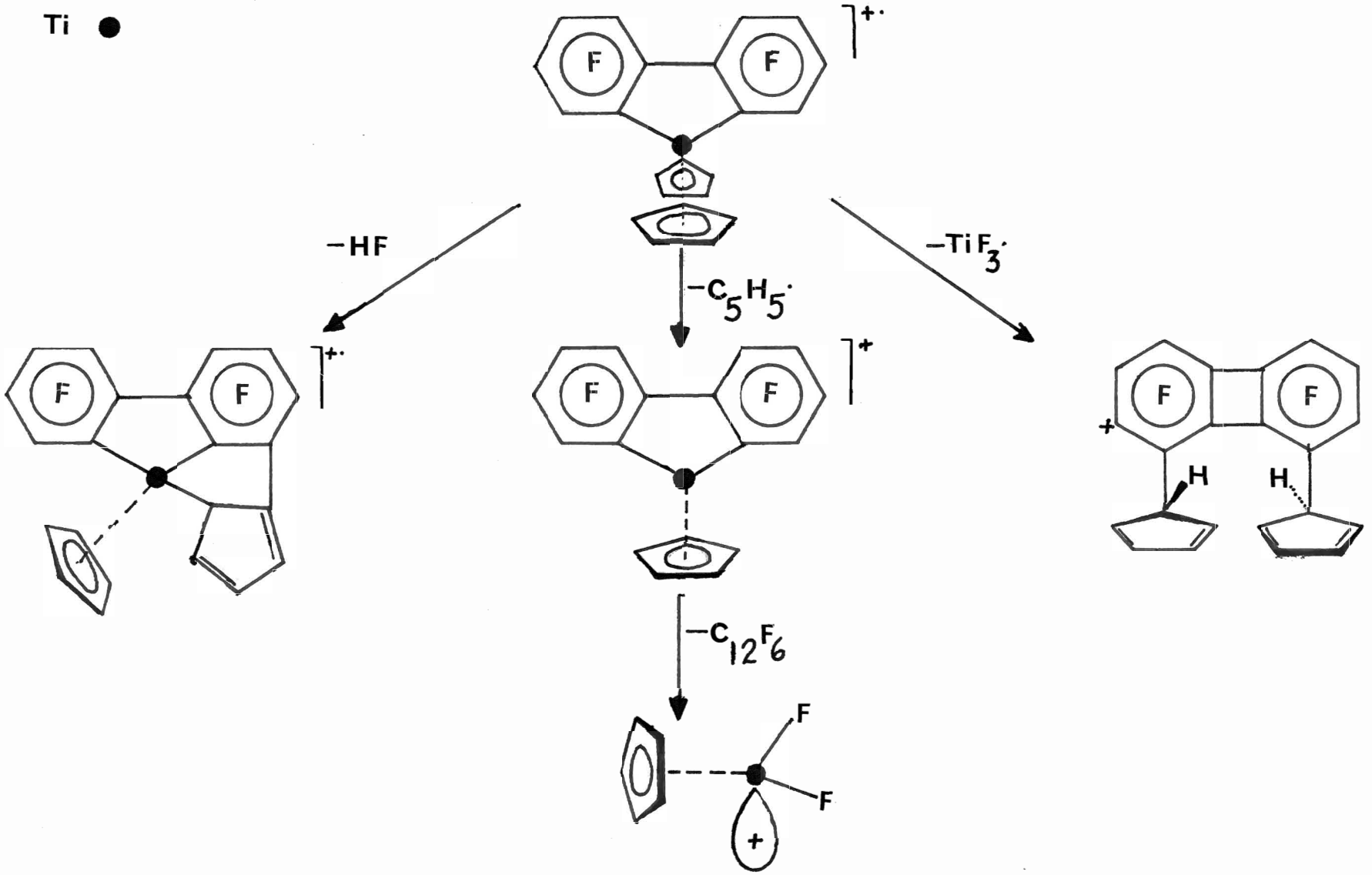

Relative Intensity (%)
100
90
80
70
60
50
40
30
20
10
50
100
150
200
250
300
350
400
450
500
m/e
$C_5H_5TiF^{+\cdot}$
$TiF_2^{+\cdot}$
$C_5H_5TiF_2^{+}$
$(M-HF)^{+\cdot}$
$M^{+\cdot}$

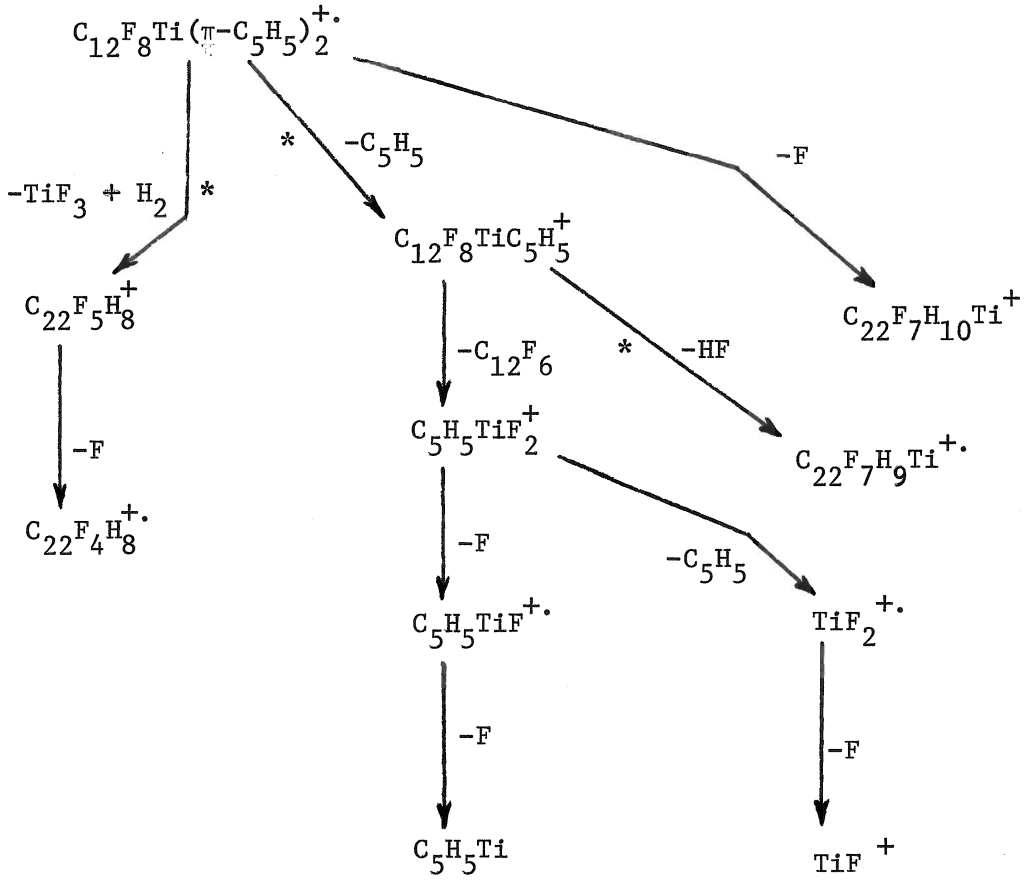
Figure 48
Fragmentation Scheme
for $(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2$

(A) Detail of significant ions
(B) Schematic

(A)



(B)


$C_{12}F_8Ti(\pi\text{-}C_5H_5)_2^{+\cdot}$
$-TiF_3 + H_2$
*
$C_{22}F_5H_8^+$
-F
$C_{22}F_4H_8^{+\cdot}$
*
$-C_5H_5$
$C_{12}F_8TiC_5H_5^+$
$-C_{12}F_6$
$C_5H_5TiF_2^+$
-F
$C_5H_5TiF^{+\cdot}$
-F
C_5H_5Ti
*
-HF
$C_{22}F_7H_9Ti^{+\cdot}$
$-C_5H_5$
$TiF_2^{+\cdot}$
-F
TiF^+
-F
$C_{22}F_7H_{10}Ti^+$

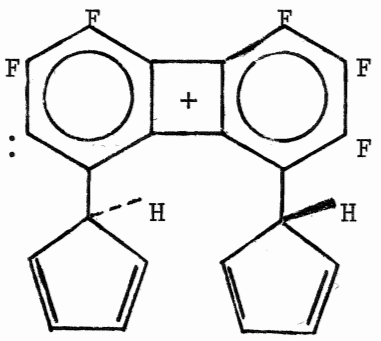
As we have already shown to a great extent, the formation of a variety of fluorocarbon ions often attends the fragmentation of such derivatives. Even though such ions are detected in low abundance the mechanism for their formation must involve some complex rearrangements which are often coupled with losses of MF_n species[8-10,13-15]. No ions were detected in these spectra corresponding to metallic fluoride fragments; nevertheless, the formation of $C_{12}F_8$-R (R = π-C_5H_5) species must at least involve rearrangements prior to loss of the metal atom. Indeed, the ions corresponding to the metal atoms themselves are present in quite reasonable intensities for the cobalt and rhodium derivatives, iridium again being the exception where no Ir^+ is observed.

(ii) $C_{12}F_8Ti(\pi\text{-}C_5H_5)_2$

The partial spectrum of this compound is also shown in Table 14. The behaviour of this compound under electron bombardment is quite different from that of the Group VIII series described earlier. The most notable difference is the wealth of ions detected corresponding to the operation of fluorine abstraction processes namely $(C_5H_5)TiF_2^+$, $(C_5H_5)TiF^+$ and TiF^+. Together, these species account for approximately 30% of the total ion current, being much more important than the simple $(C_5H_5)M$ species which dominated the spectra of the cobaltole, rhodole and iridole.

Two other basic fragmentation routes appear to be available to the molecular ion but both involve the formation of rather odd products. The first involves loss of a neutral HF molecule to give an ion whose structure and mechanism of formation is difficult to rationalize without a prior $\sigma \rightarrow \pi$ shift of the Ti-C_5H_5 bond. The second transition of interest results from loss of TiF_3 giving an ion of formula $C_{22}F_5H_{10}^+$ for which it is difficult to imagine a reasonable structure other than one related to IV below.

IV

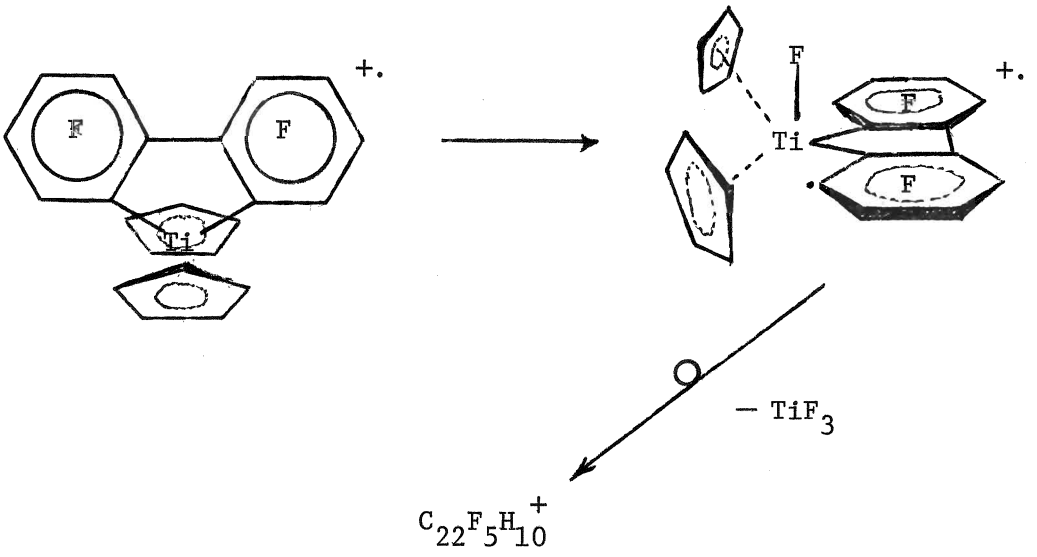


This species and others corresponding to the loss of up to 3 hydrogens from 1 are present in low abundance (ca 2-3% of total ion current).

The importance of cleavage of the Ti-C σ-bonds in the mass spectra is supported by a good deal of chemical evidence.

Alt and Rausch have studied the photolysis of dimethyl titanocene along with the related zirconocene and hafnocene[71]. They report that these compounds readily undergo photolysis with homolytic cleavage of the methyl-metal bond thus reducing the oxidation state of the metal atom. Cohen and Massey described cleavage of the same Ti-C σ bonds in $C_{12}F_8Ti(\pi\text{-}C_5H_5)_2$ using refluxing Bromine in CCl_4 or aqueous hydrogen chloride, even though the molecule has fairly high thermal stability[36].

Because of their heterocyclic nature it is extremely difficult to try to imagine the possibility of σ→π shifts of the fluoroaromatic ligand occuring as described by Hawthorne[17]. It would seem much more realistic to consider rearrangement of the molecular ion to species of higher co-ordination before breakdown as shown below.



(4) Summary of Mass Spectra and Fragmentation Mechanisms

That there is sufficient precedent to merit mass spectral studies of such fluoroaromatic systems as those described in this dissertation has been adequately demonstrated by references to earlier work. Indeed, in all the cases studied here, halogen transfer rearrangements were observed whenever vacant "d" orbitals existed on the heteroatom, the only exceptions being the series of heterocyclic derivatives of cobalt, rhodium and iridium. The latter species suffer breakdown almost exclusively by way of initial cleavage of the heteroatom-carbon sigma bonds, presumably at a rate which is too rapid to allow prior halogen transfer.

It seems redundant at this point to offer evidence in favour of either of the preferred mechanisms in addition to that already presented. Suffice it to say that based on the halogen transfers occurring with the heterocyclic species such as the phospholes and titanole it seems more reasonable to invoke expansion of co-ordination about the heteroatom than to rationalize formation of possible π-bonded intermediates suggested by the Hawthorne hypothesis[17]. Nevertheless we cannot exclude the possibility that the latter type of mechanism is in operation during fragmentation of the phosphorous derivatives described earlier even though Hawthorne has suggested that phosphorous is incapable of forming a suitable π-bonded species. It would seem

then that the study of ortho, meta and para-substituted monofluorophenyl derivatives of the elements would be useful in determining the operation of one of these mechanism although scrambling of aromatic substituents under conditions of electron impact must always be taken into account.

The fact that halogen transfers are not observed for the cobalt group (Co, Rh and Ir) and yet occur quite readily in the case of titanium could be a result of two factors. The most important consideration in light of previous observations concerning the availability of empty d-orbitals on the metal atom are the relative "d" configurations for these atoms in such heterocyclic systems. The titanium derivative represents a d^0 system with Ti in a +4 oxidation state. As a result, there is an obvious wealth of empty d-orbitals available for overlap with the ring fluorine atoms. In the cobalt group cases however, the atoms are in a +3 oxidation state representing d^6 systems. Without some detailed knowledge of orbital positions, whether hybrid or molecular, in such a system it is difficult to predict whether there are any suitable empty d-orbitals capable of accepting fluorine electrons. It would be very naive to attribute the observed behaviour to the presence of fewer empty d-orbitals on cobalt, rhodium and iridium.

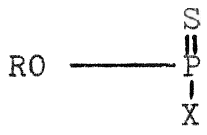
The second consideration with regards to halogen transfer concerns stability of the products formed based on bond energies. Odonnell has recently compiled a summary[79] of transition metal fluorides and though no quantitative measurements are given, the stability of MF_3 species seems to decrease in the following sequence based on M-F bond energies Ti>Co>Rh>IR. It would also be improper to try to rationalize the fluorine abstraction processes solely on this evidence since the ionized molecules being dealt with probably have bonding quite different from the comparable ground state configurations.

There is an abundance of examples in the literature[73-78] depicting the operation of Arbuzow rearrangements of the general types described in the schematic below. The equilibria normally lie far to the right in both cases and a considerable input of energy is required to reverse the process. The most notable example of this anti-Arbuzow rearrangement during electron impact was previously desc-

(i) $R_2PSR^1 + R^1X \rightleftharpoons R_2P(=S)R$, $= R'X$

(ii) $R_2PSR^1 \overset{\Delta}{\rightleftharpoons} R_2P(=S)R'$,

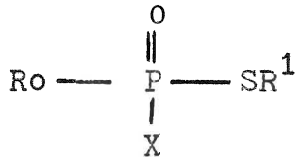
ribed in work by Cooks and Gerrard[61]. The transitions reported all involved thiophosphate molecules of the type



R_1R^1 alkyl or aryl
X halogen

which they concluded must rearrange during electron-impact-

induced fragmentation in the mass spectrometer to give species of the type



Any net gain in energy (i.e. P = O vs P = S bond formation) during rearrangement was not described as a contributing factor. No ester functions are present in our systems and these represent a direct analogy to the pure anti-Arbuzov behaviour. A more detailed study would be necessary to determine the effects of substituents on such electron-impact induced rearrangements in order to define a suitable mechanism. The thermolysis tests on a select group of compounds exhibiting this behaviour showed that the rearrangements are not thermally induced while the spectrum of a thio ester, $(C_2H_5S)PF_2(C_6F_5)_2$ gave no evidence for Arbuzov-type behaviour.

---

* Note added in proof - two of the compounds which have been studied subsequently, namely $(C_6F_5)_2PSBr$ and $(C_6F_5)_2POF$ showed behaviour consistent with the respective thionophosphinyl and phosphinyl halides described earlier.

APPENDIX A

Mass Spectra by relative abundance of the compounds described in this study. All peaks of relative abundance below 2% are neglected unless they are important to fragmentation pathways. Metastable ion analysis follows each spectrum. These will be designated m* for normal and MK for defocused metastable information (MIKES) with observed and calculated values ($\gamma = m_1/m_2$)

(1) $C_6H_5PF_2S$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
180		7.0	94	C_6H_3F	4.5
179		9.2			
178	$C_6H_5PF_2S$	88.2	78		5.5
177		5.5	77	C_6H_5	43.4
176		1.5	76		8.5
175		9.9	75		8.1
			74		9.2
159	C_6H_5PFS	2.6			
158	C_6H_4PFS	2.2	69	PF_2	22.4
146	$C_6H_5PF_2$	5.1	65		17.3
145		2.9	64		15.1
			63	PS	9.9
139	C_6H_4PS	4.4			
			52		
127	C_6H_5PF	10.7	51	C_4H_3	25.4
111		4.8			
110		7.5			
109	C_6H_5S	100.0			
108		9.2			
107		4.1			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	M-K γ OBS	γ CALC.
178	109	66.8	66.75	--	--
160	94	55.3	55.23	--	--
109	65	38.8	38.76	--	--
77	51	33.8	33.78	--	--

(2) $C_6H_5PSCl_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
215		1.3	109	C_6H_5S	25.9
214		12.5	108		2.0
213		6.2	107		3.4
212		60.7			
211		8.8	78		1.1
210	$C_6H_5PSCl_2^{35}$	100.0	77	C_6H_5	11.5
179		2.2	63	PS	4.1
178		5.4			
177		25.8			
176		7.1			
175	$C_6H_5PSCl^{35}$	68.8			
145		5.4			
144		1.1			
143	$C_6H_5PCl^{35}$	11.6			
141		1.9			
140	C_6H_5PS	2.2			
139	C_6H_4PS	15.0			
111		1.9			
110		2.0			

No metastable transitions observed.

(3) $C_6F_5PF_2S$

m/e	Ion$^+$	Relative Abundance
270		6.4
269		7.3
268	$C_6F_5PF_2S$	76.7
250		0.9
249	C_6F_5PFS	2.7
237		0.5
236	$C_6F_5PF_2$	5.0
201		2.3
200		2.7
199	C_6F_5S	20.6
182		0.9
181		1.4
180	C_6F_4S	9.1
168		0.9
167	C_6F_5	2.3
161	C_6F_3S	1.8
156		1.4
155	C_5F_5	11.0
150		0.5
149		5.0
148	C_6F_4	10.1
136	C_6F_4	0.9
130	C_5F_2S	1.0
129	C_6F_3	0.4
117	C_5F_3	5.9
112		0.5
111	C_5FS	3.2
103		0.5
102		0.5
101	PF_2S	7.3
98	C_5F_2	3.1
88		0.9
87	C_3FS	3.7
82	PFS	0.9
81	C_2F_3	2.7
79	C_5F	0.9
78		1.4
77		0.9
76		1.8
69	PF_2/CF_3	100.0
63	PS	1.8

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK OBS	MK CALC
268	180	121.0	120.90	--	--
249	167	112.2	112.00	--	--

(4) $C_6F_5PSCl_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
304		20.2	198	C_6F_5P	10.9
303		15.5	197		3.1
302		54.3	196	$C_6F_3ClS^{35}$	24.0
301		15.5			
300	$C_6F_5PSCl_2{}^{35}$	77.5	182		2.3
			181		2.3
270		19.4	180	C_6F_4S	21.7
269		3.1	179	C_6F_4P	4.7
268	$C_6F_5PCl_2{}^{35}$	23.3			
267		22.5	167	C_6F_5	5.4
266		4.7			
265	$C_6F_5PSCl^{35}$	45.7	155	C_5F_5	7.0
236		2.3	149		3.9
235		9.3	148	C_6F_4	7.8
234		6.2	147		6.2
233	$C_6F_5PCl^{35}$	32.6	146		2.3
232		2.3	145	$C_6F_2Cl^{35}$	16.3
231		3.1			
230	C_6F_5PS	16.3	118		0.8
			117	C_5F_3	31.8
202		3.1			
201		1.6	112		1.6
200		6.2	111		8.5
199	C_6F_5S	21.7	110	C_6F_2	14.7
105		21.7	82		4.7
104		3.9	81		0.8
103		69.8	80		2.3
101	$PCl_2{}^{35}$	100.0	79		15.5
			78		8.5
100		3.1	77		3.9

m/e	Ion+	Relative Abundance	m/e	Ion+	Relative Abundance
99		4.7	76		77.5
98	C_5F_2	14.0	75		1.6
			74		6.2
94		1.6			
93	C_3F_3	14.0	69	PF_2/CF_3	62.0
			68		4.7
88		4.7	67		5.4
87		13.2	66	PCl^{35}	13.2
86		5.4	65		4.7
85	$PFCl^{35}$	45.0	64		28.7
			63	PS	55.8

Metastable Transitions

m_1	m_2	m*OBS	m*CALC.	γ^{MK} OBS	γ CALC
300	233	--	--	0.79	0.78
	199	--	--	0.66	0.66
	129	--	--	0.43	0.43
	101	--	--	0.33	0.34
	69	--	--	0.23	0.23
	32	--	--	0.11	0.11
268	233	--	--	0.86	0.87
265	230	--	--	0.87	0.87
	199	--	--	0.76	0.75
	196	--	--	0.73	0.74

(5) $C_6F_5PSBr_2$

m/e	Ion$^+$	Relative Abundance
393		2.5
392		25.6
391		4.5
390		45.2
389		2.5
388	$C_6F_5PSBr_2^{79}$	25.1
360		1.4
359		0.3
358		2.0
357		0.3
356	$C_6F_5PBr_2^{79}$	1.4
313		5.9
312		9.5
311		98.9
310		9.8
309	$C_6F_5PSBr^{79}$	100.0
280		1.1
279		9.8
278		1.1
277	$C_6F_5PBr^{79}$	10.0
243		1.1
242		9.8
241		1.1
240	$C_6F_3Br^{79}S$	9.8
232		4.5
231		6.7
230	C_6F_5PS	69.8

m/e	Ion$^+$	Relative Abundance
193		5.9
192		0.8
191		12.0
190	PBr^{79} (58.5%)	0.8
189	$C_6F_2Br^{79}$ (41.5%)	8.9
181		1.1
180	C_6F_4S	9.2
179		4.7
149		1.7
148	C_6F_4	10.3
144		2.8
142	$PSBr^{79}$	2.7
131		7.9
129	$PFBr^{79}$	8.1
117	C_5F_3	6.7
111		1.7
110	C_6F_2	7.3
98	C_5F_2	2.8
93	C_3F_3	3.3
81	Br 81/C_2F_3	5.0
80		2.2
79	Br^{79}	4.5
78		2.8
69	PF_2/CF_3	18.9
65		3.9
64		2.8
63	PS	54.4

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γ OBS	MK γ CALC
392/390/388	311/309	246.6	246.41	--	--
311	230		170.10	--	--
		171.1			
230	199		172.18		

(6) $C_6F_5(CH_3)PSF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
266		5.9	180	C_6F_4S	30.3
265		9.6			
264	$C_6F_5(CH_3)PSF$	100.0	175	$C_7F_3H_3P$	6.5
251		2.2	168		3.5
250		2.8	167	C_6F_5	2.9
249	C_6F_5PSF	25.8			
			164		1.6
233		1.4	163	$C_7F_4H_3$	10.5
232	$C_6F_5(CH_3)PF$	7.6	162		4.8
231		2.8	161	C_6F_3S	6.3
218		2.8	159		3.5
217	C_6F_5PF	25.0			
			150		1.3
201		1.4	149		1.7
200		12.7	148	C_6F_4	4.7
199	C_6F_5S	2.6			
			144		0.9
182		2.6	143	$C_7F_3H_2$	6.3
181	$C_7F_5H_2$	9.0			
130		3.6	88	PF_3	5.6
129	C_6F_3	31.6	87		4.3
128		5.1	86		2.0
127	$C_2F_3H_3P$	60.8			
			83		2.1
119		1.1	82	PFS	3.4
118		1.9	81		1.7
117	C_5F_3	16.3	80		1.7
			79		7.3
112		2.3	78	CH_3PS	1.9
111		5.1	77	CH_2PS	17.6
110	C_6F_2	4.9	76		5.2

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
109		10.8	75		5.2
108		1.6	74		3.6
107	PF_4	3.9			
			69	PF_2/CF_3	65.5
99		5.2	65	CH_3PF	67.3
98		8.2	63	PS	10.2
97	CH_3PFS	20.1			
			51	HPF	15.3
93	C_3F_3	9.3			

Metastable Transitions

m_1	m_2	m*OBS	M*CALC	γ OBS	MK γCALC
264	217	--	--	0.83	0.82
	180	--	--	0.68	0.68
	168	--	--	0.64	0.64
	129	--	--	0.48	0.49
	117	--	--	0.44	0.44
	93	--	--	0.35	0.35
	69	--	--	0.28	0.26
	46	--	--	0.18	0.17
	32	--	--	0.13	0.12
249	180	--	--	0.73	0.72
	155	--	--	0.63	0.62
	117	--	--	0.47	0.47
200	168	--	--	0.85	0.84
	129	--	--	0.65	0.65

(7) $C_6F_5(C_2H_5)PSF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
280		6.0	130		7.7
279		10.2	129	C_6F_3	34.9
278	$C_6F_5(C_2H_5)PSF$	71.2			
			119		3.2
252		5.2	118		2.6
251		7.7	117	C_5F_3	13.7
250	C_6F_5PHSF	62.3			
249		10.5	111		6.0
			110	C_6F_2	4.3
246	$C_6F_5(C_2H_5)PF$	6.0			
245		5.0	99		2.6
			98	C_5F_2	6.8
218		12.3			
217	C_6F_5PF	100.0	93	C_3F_3	7.4
182		2.6	88	PF_3	5.8
181		6.1	87		3.6
180	C_6F_4S	21.3			
			83	HPFS	11.2
169		2.6	82	PFS	3.8
168	C_6F_5H	12.3			
			80		3.1
131		3.0	79	C_2H_5PF	10.8
77		4.3	69	PF_2/CF_3	55.8
76		10.0	67		6.8
75		2.9	63	PS	10.2

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γ^{MK} OBS	γ^{MK} CALC
278	250	--	--	0.87	0.89
	180	--	--	0.64	0.65
	168	--	--	0.60	0.60
	69	--	--	0.25	0.25
	28	--	--	0.10	0.10
250	217	--	--	0.86	0.87
	180	--	--	0.70	0.72
	168	--	--	0.66	0.67
	129	--	--	0.53	0.52
	117	--	--	0.46	0.47
	83	--	--	0.33	0.33
	32	--	--	0.13	0.13
	19	--	--	0.77	0.76
217	186	--	--	0.86	0.86
	129	--	--	0.59	0.59
	69	--	--	0.31	0.32
	31	--	--	0.15	0.14

(8) $C_6F_5(t\text{-}C_4H_9)PFS$

m/e	Ion$^+$	Relative Abundance
307		0.4
306	$C_6F_5(C_4H_9)PFS$	3.2
291	$C_6F_5(C_3H_6)PFS$	0.4
274	$C_6F_5(C_4H_9)PF$	0.4
273		1.1
271		0.2
269		0.2
267	$(C_6F_4)(C_4H_8)PS$	0.2
264	$C_6F_5PSF(CH_3)$	0.5
263		0.2
262		0.3
249		0.9
248	$(C_6F_3)(C_4H_8)PS$	1.6
247		0.9
246		0.2
219		0.4
218		0.3
217	C_6F_5PF	2.7
181		0.7
180	C_6F_4S	1.0
169		0.8
168	C_6F_5H	0.8
131		1.2
129	C_6F_3	0.6
119		1.7
76	C_4H_9F	2.3
69	PF_2/CF_3	6.6
58		3.2
57	C_4H_9	100.0
56	C_4H_8	11.3
55	C_4H_7	2.3

No metastable transitions detected.

(9) $C_6H_5(C_6F_5)PSF$

m/e	Ion$^+$	Relative Abundance
329		0.4
328		2.2
308		0.5
307	$C_6H_5(C_6F_5)PS$	1.2
306		0.3
305		0.1
295		0.3
294	$C_{12}H_5F_6P$	2.2
293		4.8
289		0.8
288		0.2
287	$C_{12}H_4F_4PS$	1.0
276		0.2
275	$C_{12}H_5F_5P$	0.7
274		0.4
273		0.2
258		0.2
257		0.6
256	$C_{12}H_5F_4P$	2.7
255		0.3
251		0.1
250		0.1
249	C_6F_5PSF	0.5
245		0.2
244	$C_{12}H_5F_5$	1.2
243		0.2
242		0.3

m/e	Ion$^+$	Relative Abundance
327		5.6
326	$(C_6H_5)(C_6F_5)PSF$	40.8
218		0.6
217	C_6F_5PF	5.9
207		0.2
206	$C_{12}H_5F_3$	0.7
205		0.5
204		0.4
200		0.2
199	C_6F_5S	0.3
198		0.3
194		0.1
193	$C_{11}H_4F_3$	0.5
192		0.2
182		0.2
181		0.3
180	C_6F_4S	2.0
161		0.5
160		0.5
159	C_6H_5PSF	4.3
158		0.4
156		0.1
155	$C_{11}H_4F$	0.4
149		0.2
148	C_6F_4	0.5

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
			139		0.1
225		0.5	138	C_6H_3PS	0.6
224	$C_{12}H_4F_4$	2.2			
130		0.6	94		0.1
129	C_6F_3	5.3	93	C_3F_3	1.2
128		6.3			
127		100.0	87		0.6
118		0.2	78		1.5
117	C_5F_3	1.9	77	C_6H_5	23.4
			76		1.3
111		1.2	75		2.7
110	C_6F_2	1.5	74		1.9
109	C_6H_5S	13.8			
108		1.7	70		0.2
107		2.5	69	PF_2/CF_3	13.3
102		0.1	65		3.8
101	PF_2S	1.5	63	PS	3.5
100		0.3			
99		1.1	52	C_4H_4	1.0
98	C_5F_2	0.9	51	C_4H_3	18.2

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γ OBS	MK γ CALC
326	159	--	--	0.49	0.49
	127	49.5	49.48	0.37	0.39
	50	--	--	0.16	0.15
307	288	270.0	270.18	--	--
	167	91.0	90.84	--	--
127	77	46.8	46.69	--	--
109	65	38.8	38.76	--	--
77	51	33.8	33.78	--	--

(10) $(C_6F_5)_2PFS$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
419		0.7	219		0.5
418		3.0	218		7.9
417		7.0	217	C_6F_5PF	100.0
416	$(C_6F_5)_2PFS$	41.3			
			201		0.3
400		0.5	200		0.7
399		1.4	199	C_6F_5S	3.0
398		3.3			
397	$(C_6F_5)_2PS$	13.5	182		0.5
			181		0.7
385		0.7	180	C_6F_4S	6.3
384	$(C_6F_5)_2PF$	3.0			
			167	C_6F_5	0.5
379		0.5			
378	$C_{12}F_9PS$	0.9	161	C_6F_3S	0.7
			155		0.7
366		0.5			
365	$C_{12}F_{10}P$	1.4	149		0.7
			148	C_6F_4	0.5
330		0.5			
329		0.3	130		1.4
328	$C_{12}F_8S$	4.0	129	C_6F_3	17.3
310		0.2	117	C_5F_3	0.9
309	$C_{12}F_7S$	1.9			
			111		0.7
297		0.7			
296	$C_{12}F_8$	0.9	107	PF_4	1.4
251		0.7			
250		1.4	69	PF_2/CF_3	12.8
249	C_6F_5PFS	15.4			
			63	PS	0.9

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	MK γ CALC
416	217	113.2	113.19	--	--
384	365	346.8	346.94	--	--
217	129	76.8	76.69	--	--

(11) $(C_6F_5)_2PSCl$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
436		1.7	278	$C_{11}F_6S$	1.3
435		4.8	277	$C_{12}F_7$	1.3
434		24.8			
433		10.9	267		4.8
432	$(C_6F_5)_2PSCl^{35}$	54.9	266		1.7
			265	$C_6F_5PSCl^{35}$	14.3
402		3.0			
401		1.7	259	$C_{11}F_5S$	1.7
400	$(C_6F_5)_2PCl^{35}$	8.3	258	$C_{12}F_6$	1.3
399		2.6			
398		6.5	249	C_6F_5PSF	5.7
397	$(C_6F_5)_2PS$	40.9			
			246	$C_{11}F_6$	1.7
366		1.3			
365	$(C_6F_5)_2P$	7.0	236		3.5
			235		38.7
330		1.3	234		9.6
329		1.7	233	$C_6F_5PCl^{35}$	100.0
328	$C_{12}F_8S$	8.3			
			231		1.7
309	$C_{12}F_7S$	1.7	230	C_6F_5PS	7.4
297		1.7	227	$C_{11}F_5$	2.6
296	$C_{12}F_8$	5.2			
			218		1.3
290	$C_{12}F_6S$	1.3	217	C_6F_5PF	10.0
201		0.7	142	C_6F_2S	1.3
200		1.3	141	C_6F_2P	2.2
199	C_6F_5S	8.7			
198	C_6F_5P	5.2	130	C_5F_2S	2.2
197		1.3	129	C_6F_3	15.2

m/e	Ion+	Relative Abundance	m/e	Ion+	Relative Abundance
196	$C_6F_3SCl^{35}$	6.1			
			118		1.3
182		1.3	117	C_5F_3	16.5
181		2.2			
180	C_6F_4S	13.5	111		4.4
179	C_6F_4P	3.0	110	C_6F_2	10.0
167	C_6F_5	2.2	98	C_5F_2	6.5
161	C_6F_3S	2.2	93	C_3F_3	7.8
155	C_5F_5	5.7	87		9.6
			86		1.3
149		2.6	85	$PFCl^{35}$	26.1
148	C_6F_4	4.8			
147		13.9	79		6.1
146		3.0	76		1.3
145	$C_6F_2Cl^{35}$	37.0	74	C_3F_2	1.7
			69	PF_2/CF_3	56.5
			66		1.7
			65		2.2
			64		1.7
			63	PS	31.3

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	γ CALC
432	397	--	--	0.89	0.92
	365	--	--		0.85
	296	--	--	0.70	0.69
432	265	--	--	0.60	0.61
	233	125.8	125.67	0.54	0.54
	180	--	--	0.42	0.42
	167	--	--	0.39	0.39
	129	--	--	0.32	0.30

m_1	m_2	m*OBS	m*CALC	γOBS	MK γ CALC
	98	--	--	0.23	0.23
	69	--	--	0.15	0.16
	63	--	--		0.15
	32	--	--	0.08	0.07
233	145	90.3	90.24	--	--

(12) $(C_6H_5)_2POF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
222		1.3	115	C_5H_5PF	2.0
221		10.9			
220	$(C_6H_5)_2POF$	51.1	110	$(C_6H_5)_2POF^{++}$	2.6
219	$C_{12}H_9POF$	100.0			
			109.5	$C_{12}H_9POF^{++}$	4.5
201		1.1			
200		4.0	106	C_6H_3P	3.0
199	$C_{12}H_8PO$	22.7			
			78	C_6H_6	8.0
155		0.7	77	C_6H_5	40.2
154		2.4	76	C_6H_4	7.5
153		5.7	75		6.2
152	$C_{12}H_8$	14.9	74		5.4
151		3.7			
150		1.4	67	HPOF	3.5
			63	C_5H_3	4.2
128		2.2			
127	C_6H_5PF	18.9	52		6.2
126		1.7	51	C_4H_3	70.2
			50	C_4H_2	18.7

No metastable transitions observed.

(13) $C_6F_5(CH_3)POF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
250		1.2	181	$C_7F_5H_2$	20.9
249		11.2	180		1.7
248	$C_6F_5(CH_3)POF$	100.0	179		1.5
247		15.5			
246		75.6	169		1.7
			168	C_6F_5H	16.9
234		3.8	167	C_6F_5	14.3
233	C_6F_5POF	39.5	166		0.9
232		5.0	165		5.8
231	$C_6F_5PF(CH_2)$	48.9	164	C_6F_4O	36.8
230		4.0	163	$C_7F_4H_3$	13.7
229	$C_6F_5PO(CH_3)$	13.2	162	$C_7F_4H_2$	15.3
228		1.7	161		3.5
227		1.5	160		0.8
226		2.7	159		1.5
217	C_6F_5PF	2.9	155	C_5F_5	2.9
216		0.4	153	C_5F_4OH	5.2
215	C_6F_5POH	2.3			
			150		1.5
206		0.6	149		2.3
205	C_5F_5PF	5.4	148	C_6F_4	12.8
204		0.8			
203		10.6	146		2.1
			145	C_6F_3O	6.8
185		2.9	144		0.7
184	C_6F_5OH	30.4	143	$C_7F_3H_2$	3.5
183		8.1			
182		3.3	137	C_5F_4H	9.3
136	C_5F_4	6.6	93	C_3F_3	12.0
132		3.5	82		0.9

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
131	$C_6F_3H_2$	4.9	81	CH_3POF	30.6
130		1.8	80		2.5
129	C_6F_3	7.2	79	HCPOF	41.8
			78		1.7
119		4.3	77		1.9
118		3.7	76		0.8
117	C_5F_3	30.1	75		2.8
115		3.3	69	PF_2/CF_3	34.7
			68		1.0
113		1.9	67	HPOF	26.9
112	$C_6F_2H_2$	3.1	66		1.2
111		1.5	65	CH_3PF	31.8
110	C_6F_2	1.7	64		1.7
			63	C_2F_2H	35.0
105		2.7			
			58	HPO	3.1
99		7.3			
98	C_5F_2	7.1			

No metastable transitions observed.

(14) $C_6F_5(t\text{-}C_4H_9)POF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
292		0.6	277		0.6
291		9.2	276		5.6
290	$C_6F_5(tC_4H_9)POF$	34.4	275	$C_6F_5(C_3H_6)POF$	41.3
289		3.8			
288		2.3	255	$C_6F_5(C_3H_5)PO$	6.1
236		1.2	148		1.2
235		11.5	147		4.6
234	C_6F_5PHOF	15.5	146	C_6F_3OH	8.6
233	C_6F_5POF	4.8	145		1.2
			144	$C_7F_3H_3$	3.7
218		1.3			
217	C_6F_5PF	15.3	138		0.8
			137		3.1
210		0.6	136	C_5F_4	5.7
209	$C_6F_5(C_3H_6)$	2.5			
			131		2.5
206		0.4	130		1.2
205	C_5F_5PF	3.3	129	C_6F_3	9.2
192		0.4	119		1.2
191	$C_7F_4H_2P$	1.9	118		3.1
			117	C_5F_3	36.7
189		1.0			
188		2.3	100		0.6
187	$C_6F_4(C_3H_3)$	5.2	99	C_5F_2H	11.7
			98		2.5
182		1.3			
181	$C_7F_5H_2$	1.1	93	C_3F_3	7.8
169		3.4	81		2.7
168		13.4	80		1.3
167	C_6F_5	14.2	79		2.5

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
165		1.9	69	PF_2/CF_3	6.5
164	C_6F_4O	21.0			
163	$C_7F_4H_3$	2.1	58		54.3
			57	C_4H_9	100.0
			56	C_4H_8	93.3
			55	C_4H_7	57.0
			53	C_4H_5	5.7

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	γCALC
255	235	216.5	216.57	--	--
129	69	37.0	36.91	--	--
117	69	40.5	40.69	--	--
57	41	29.5	29.49	--	--

(15) $C_6F_5(C_6H_5)POF$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
312		0.8	245		0.6
311		8.2	244	$C_{12}F_5H_5$	3.2
310	$C_6F_5(C_6H_5)POF$	41.8	243		1.6
309		3.0	242	$C_{12}F_5H_3$	4.2
			241		1.6
295		0.8	240	$C_{12}F_5H$	6.2
294		4.4			
293		5.2	226		0.4
292		5.6	225		3.4
291	$C_6F_5(C_6H_5)PO$	33.2	224	$C_{12}F_4H_4$	12.0
290	$C_6F_5C_6H_4PO$	56.2	223		6.4
289		1.0	222	$C_{12}F_4H_2$	8.2
			221		1.0
276		0.8			
275		1.0	218		0.6
274		0.4	217	C_6F_5PF	3.6
273		0.8			
272		2.4	213	$C_{11}F_4H_4$	2.0
271	$C_{12}F_4H_4PO$	9.2	212		0.6
270		0.4	211		1.2
262	$C_{12}F_3H_4PO$	0.8	207		1.0
			206	$C_{12}F_3H_5$	7.8
255	$C_{12}F_4H_4P$	1.0	205		5.0
			204		2.0
199		0.6	107	PF_4	3.2
198	C_6F_5P	2.4			
			101		2.4
194		2.2	100		0.4
193	$C_{11}F_3H_3$	11.4	99		1.6
192		1.6	98	C_5F_2	1.2

m/e	Ion$^+$	Relative Abundance
176		0.8
175		4.8
174	$C_{11}H_2H_4$	4.6
173		1.2
169		0.4
168		1.8
167	C_6F_5	3.0
166		0.4
165		3.6
164		2.6
149		0.4
148	C_6F_4	1.6
144		1.6
143	C_6H_5POF	9.8
142		0.8
141		0.6
131		0.8
130		1.6
129	C_6F_3	5.4
128		2.8
127	C_6H_5PF	24.4
118		0.6
117	C_5F_3	5.2

m/e	Ion$^+$	Relative Abundance
93	C_3F_3	1.8
88	PF_3	0.8
78		9.8
77	C_6H_5	100.0
76		12.2
75		8.2
74		3.4
70		0.8
69	PF_2/GF_3	15.0
68	H_2POF	11.4
67		0.8
66	POF	6.2
65		1.4
64		2.8
63		0.8
53		0.6
52		5.8
51	C_4H_3	86.0

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	MK γ CALC
310	290	271.2	271.29	--	--
	101	32.9	32.91	--	--
309	262	222.8	222.15	--	--
291	271	252.6	252.37	--	--
290	271		253.24	--	--
290	240	199.1	198.62	--	--
271	117	50.5	50.51	--	--
175	77	33.9	33.88	--	--
143	77	41.5	41.46	--	--

(16) $(C_6F_5)_3PF_2$

m/e	Ion$^+$	Relative Abundance
572		0.2
571		0.9
570	$(C_6F_5)_3PF_2$	3.6
553		0.2
552		1.2
551	$(C_6F_5)_3PF$	4.3
533		0.1
532	$(C_6F_5)_3P$	0.3
513	$(C_6F_5)_2PC_6F_4$	0.2
482	$C_{18}F_{14}$	0.1
463	$C_{18}F_{13}$	0.1
445		0.1
444	$C_{18}F_{12}$	0.2
316		0.2
315	$C_{12}F_9$	0.3
297		0.4
296	$C_{12}F_8$	2.2
277		0.3
276		0.2
275	$C_{15}F_5$	0.5
266		0.3
265	$C_{11}F_7$	1.5
432	$C_{17}F_{12}$	0.2
405		1.4
404		13.0
403	$(C_6F_5)_2PF_2$	100.0
386		0.1
385		0.8
384	$(C_6F_5)_2PF$	3.1
366		0.3
365	$(C_6F_5)_2P$	1.7
335		0.3
334	$C_{12}F_{10}$	1.6
328		0.2
327	$C_{12}F_8P$	0.2
218		0.6
217	C_6F_5PF	5.5
215	$C_{10}F_5$	0.3
202		0.6
201.5	$(C_6F_5)_2PF_2^{++}$	2.5
186	C_6F_6	0.5
168		1.3
167	C_6F_5	5.4
149		0.8
148	C_6F_4	5.3

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
260		0.2			
			131		0.3
258	$C_{12}F_6$	0.4	130		0.8
			129	C_6F_3	5.9
256		0.6			
255	$C_6F_5PF_3$	5.6	118		0.9
			117	C_5F_3	8.0
			107	PF_4	2.1
			99		0.7
			98	C_5F_2	2.1
			94		0.2
			93	C_3F_3	2.6
237		0.3			
236	$C_6F_5PF_2$	2.3	89		0.1
			88	PF_3	1.3
228		0.1			
227	$C_{11}F_5$	0.7	70		0.3
			69	PF_2/CF_3	21.0

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	γ CALC
570	403	285.0	284.92	--	--
	217	82.6	82.61	--	--
403	265	174.3	174.26	--	--
	255	161.5	161.35	--	--
384	365	347.1	346.94	--	--
334	148	65.6	65.58	--	--
217	129	76.8	76.69	--	--

(17) $(C_6F_5)_2(C_2H_5S)PF_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
464	$(C_6F_5)_2PF_2(SC_2H_5)$	0.0	398	$(C_6F_5)_2PHS$	6.2
			397		5.9
445	$(C_6F_5)_2PF(SC_2H_5)$	0.3			
			386		0.3
435	$(C_6F_5)_2PF_2S$	0.3	385		1.3
			384	$(C_6F_5)_2PF$	2.1
428		0.3			
427		0.5			
426	$(C_6F_5)_2P(SC_2H_5)$	2.9			
417		0.4	366		0.7
416	$(C_6F_5)_2PFS$	0.8	365	$(C_6F_5)_2P$	4.3
405		1.1	329		0.3
404		11.3	328	$C_{12}F_8S$	1.7
403	$(C_6F_5)_2PF_2$	100.0			
			312		0.3
401		4.7	311		1.6
400	$(C_6F_5)_2PH_3S$	24.0			
399		1.4			
297		0.7	181		0.4
296	$C_{12}F_8$	3.1	180	C_6F_4S	1.8
266		0.5	168		1.8
265	$C_{11}F_7$	3.0	167	C_6F_5	10.5
256		0.7	165		1.3
255	$C_6F_5PF_3$	11.0	164	$C_7F_4H_4$	13.3
250		0.4	149		1.8
249	C_6F_5PFS	1.2	148	C_6F_4	7.9
247		0.2	146		0.4
246	$C_{11}F_6$	0.7	145	$C_7F_3H_4$	2.6

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
237		0.5	137		0.5
236	$C_6F_5PF_2$	4.3	136	C_5F_4	4.4
234		1.2	131		1.9
233	$C_{12}F_3S$	4.4	130		2.5
			129	C_6F_3	19.6
231		0.8			
230	C_6F_5PS	1.2	118		2.3
			117	C_5F_3	18.5
228		0.3			
227	$C_{11}F_5$	1.0	111		1.4
			110	C_6F_2	2.2
218		4.6			
217	C_6F_5PF	76.4	107	PF_4	4.8
205	C_5F_5PF	1.7	101	PF_2S	1.6
200		0.8	99		0.6
199	C_6F_5S	3.0	98	C_5F_2	4.7
198	C_6F_5P	4.1			
			95		0.6
94		0.4	63	PS	6.4
93	C_3F_3	4.7	62		0.7
			61	SC_2H_5	4.6
79		2.5	60		5.2
			59		3.2
69	PF_2/CF_3	41.7	58		2.1
			51		1.1

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	γ CALC
464	416	373.0	372.97	--	--
403	217	116.9	116.85	--	--
365	296	240.1	240.04	--	--

MK

m_1	m_2	m*OBS	m*CALC	γOBS	γ CALC
236	167	117.9	118.17	--	--
217	129	76.8	76.69	--	--
205	129	81.2	81.18	--	--

(18) $C_6F_5N(CH_3)_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
213		0.4	194	C_6F_5NCH	17.8
212		7.3	193		0.6
211	$C_6F_5N(CH_3)_2$	87.0	192	$C_6F_4N(CH_3)_2$	1.1
210	$C_6F_5N(C_2H_5)$	100.0	191		0.5
209		1.5	189		0.3
208		5.1	189		0.3
197		0.5	183		0.9
196	$C_6F_5NCH_3$	3.5	182		4.2
195	$C_6F_5NCH_2$	10.3	181	$C_7F_5H_2$	6.8
177	$C_6F_4N(CH_3)$	1.2	127		0.3
176		1.6	126	$C_7F_2H_4$	1.4
175		0.5	125		0.2
174		3.0	124	$C_7F_2H_2$	0.5
168		2.0	120		0.2
167	C_6F_5	4.2	119		0.9
			118		0.3
164		0.9	117	C_5F_3	1.8
163	$C_7F_4H_3$	4.2			
			106		0.5
156		0.8	105.5	$C_6F_5N(CH_3)_2$ $^+$	0.9
155	C_5F_5	1.5	105		0.3
150		0.7	99	C_5F_2H	1.3
149	C_6F_4H	1.8			
			93	C_3F_3	0.5
145		0.4			
144		0.4	69	CF_3	0.6
143	$C_7F_3H_2$	0.4			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γOBS MK	γ CALC
211	210	--	--	0.99	1.00
	182	--	--	0.86	0.86
	177	--	--	0.84	0.84
	163	--	--	0.77	0.77
	117	--	--	0.56	0.56
	93	--	--	0.43	0.44
	69	--	--	0.34	0.33
210	181	--	--	0.87	0.86
	167	--	--	0.81	0.80
	155	--	--	0.75	0.74
	117	--	--	0.55	0.56
	93	--	--	0.44	0.44
	43	--	--	0.21	0.21
	29	--	--	0.13	0.14
195	155	--	--	0.80	0.80
	144	--	--	0.74	0.74
	119	--	--	0.61	0.61
	113	--	--	0.58	0.58
	101	--	--	0.52	0.52
	93	--	--	0.48	0.48
	43	--	--	0.22	0.22
	31	--	--	0.15	0.16
	19	--	--	0.10	0.10
194	163	--	--	0.85	0.84
	144	--	--	0.76	0.75
	117	--	--	0.60	0.60
	99	--	--	0.50	0.51
	93	--	--	0.48	0.48
	69	--	--	0.36	0.36
	42	--	--	0.22	0.22
	31	--	--	0.16	0.16

MK

m_1	m_2	m*OBS	m*CALC	γOBS	γ CALC
181	155	--	--	0.88	0.86
	148	--	--	0.82	0.82
	137	--	--	0.76	0.76
	131	--	--	0.73	0.72
	117	--	--	0.65	0.65
	114	--	--	0.63	0.63
	93	--	--	0.51	0.51

(19) $C_6F_5P(CH_3)_2$

m/e	Ion$^+$	Relative Abundance
230		0.6
229		8.8
228	$C_6F_5P(CH_3)_2$	100.0
227		1.0
215		0.2
214		2.5
213	$C_6F_5P(CH_3)$	31.5
212		5.3
211	C_6F_5PCH	66.9
210		1.3
209		2.4
200		0.5
199	C_6F_5PH	5.6
198		0.9
195		0.4
194		0.5
193	$C_7F_4H_2P$	1.1
192		0.3
191		0.3
183		0.2
182		3.4
181	$C_7F_5H_2$	44.1
180		3.1
179		1.9
169		0.9
168	C_6F_5H	9.6
167		0.5
164		0.6

m/e	Ion$^+$	Relative Abundance
163	$C_7F_4H_3$	4.4
162		0.8
161	C_7F_4H	3.9
155		0.6
150	$C_6F_4H_2$	1.3
149		0.9
148	C_6F_4	1.3
145		1.1
144	$C_7F_3H_3$	9.0
143	$C_7F_3H_2$	9.2
142		5.1
141		1.4
138		0.8
137		2.0
129	C_6F_3	1.6
127		0.2
126		0.9
125	$C_7F_2H_3$	8.0
124		2.0
123	C_7F_2H	5.3
119		0.9
118		1.3
117	C_5F_3	4.6
114		0.5
113		0.6
112	$C_6F_2H_2$	1.0

(21) $C_6F_5P(O)(CH_3)_2$

m/e	Ion$^+$	Relative Abundance
246		0.6
245		7.2
244	$C_6F_5PO(CH_3)_2$	54.4
229	$C_6F_5PO(CH_3)$	100.0
228		2.2
227		1.1
226		1.1
225		2.2
214		1.7
213	$C_6F_5P(CH_3)$	3.3
211		3.9
210		2.2
209	$C_6F_4PO(CH_2)$	5.0
199	C_6F_5PH	1.1
183		0.6
182		0.6
181	$C_7F_5H_2$	7.2
179		2.2
169		1.7
168	C_6F_5H	1.1
164		2.8
163	$C_7F_4H_3$	13.9
162		1.7
161		2.8
160		5.5
159		2.8
242		0.6
231		0.6
230	$C_6F_5PH(O)CH_3$	6.1
145		0.6
144		3.3
143	$C_7F_3H_2$	10.6
142		0.6
141		1.7
133		1.1
132		3.9
131		1.1
130		0.6
129	C_6F_3	11.1
125	$C_7F_2H_3$	1.1
124		0.6
123		2.8
119		0.6
118		0.6
117	C_5F_3	11.1
114		0.6
113		3.9
112		1.1
111	C_6F_2H	11.7
110	C_6F_2	3.3
99		4.4
98	C_5F_2	5.0
96		0.6
95		0.6

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
111	C_6F_2H	5.1	76		0.5
110	C_6F_2	5.7	75	C_3F_2H	7.1
			74	C_3F_2	1.7
107		0.5			
106		0.5	69	CF_3/PF_2	29.9
105	C_4F_3	1.3			
104		0.7	65		15.7
103		0.6			
			62		0.7
100		0.7	61	$(CH_3)_2P$	4.6
99	C_5F_2H	6.6	60		0.9
98	C_5F_2	2.5	59	C_2H_4P	5.0
			58		2.0
94		1.2	57	C_2H_2P	4.6
93	C_3F_3	5.4			
92		1.4	51		1.6
91		0.7			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γ OBS	MK γ CALC
228	181	143.7	143.69	0.80	0.79
	168	--	--	0.74	0.76
	163	116.5	116.53	0.72	0.72
	144	--	--	0.63	0.62
	119	62.2	62.11	0.52	0.51
	93	--	--	0.41	0.39
	69	--	--	0.30	0.31
	65	--	--	0.29	0.28
	45	--	--	0.20	0.20
	31	--	--	0.14	0.14
	15	--	--	0.07	0.07

MK

m_1	m_2	m*OBS	m*CALC	γOBS	γCALC
213	193	174.9	174.88	0.91	0.91
	144	97.5	97.35	0.68	0.68
	125	73.4	73.36	0.59	0.59
	93	--	--	0.44	0.44
	69	22.4	22.35	0.32	0.32
211	161	122.8	122.85	0.77	0.76
	142	95.7	95.56	0.67	0.67
	123	71.7	71.70	0.59	0.58
	93	41.1	40.99	0.45	0.44
	69	22.7	22.56	0.33	0.33
199	110	60.9	60.80	--	--
181	131	94.8	94.81	0.73	0.72
	93	47.9	47.78	0.52	0.51
	69	--	--	0.39	0.38
168	105	66.6	66.63	0.64	0.63
	99	58.3	58.34	0.59	0.59
	75	33.5	33.48	0.45	0.45
	56	--	--	0.33	0.33
144	125	108.5	108.51	0.85	0.87
	75	--	--	0.53	0.52
	69	--	--	0.49	0.48
143	93	60.6	60.48	0.66	0.65
	75	39.3	39.34	0.53	0.52
	69	33.2	33.29	0.49	0.48
142	123	106.5	106.54	--	--
137	69	34.8	34.75	--	--
131	69	36.3	36.34	--	--
125	99	78.4	78.41	--	--
	75	45.1	45.00	--	--
110	79	56.7	56.74	--	--

(20) $C_6F_5As(CH_3)_2$

m/e	Ion$^+$	Relative Abundance
274		1.0
273		9.4
272	$C_6F_5As(CH_3)_2$	93.8
259		1.0
258		9.4
257	$C_6F_5As(CH_3)$	100.0
256		5.1
255	C_6F_5AsCH	46.9
243		5.7
242	C_6F_5As	25.0
238		1.6
237	$C_7F_4H_2As$	6.8
233		1.5
232	$C_6F_3As(C_2H_4)$	35.0
224		0.5
223	C_6F_4As	7.0
218		1.5
217	C_7F_3HAs	24.4
205	C_6F_3HAs	2.7
203		3.0
202	$C_4F_4H_3As$	6.3
187		2.1
186	C_6F_2HAs	6.8
185		1.8
184		8.3
182		7.3
181	$C_7F_5H_2$	72.4
171	$C_3F_3H_3As$	7.5
169		6.7
168	C_6F_5H	8.9
164		3.1
163	$C_7F_4H_3$	25.9
162		2.1
161	C_7F_4H	12.0
153		1.6
152	$C_3F_2H_3As$	20.7
144	$C_7F_3H_3$	13.6
143	$C_7F_3H_2$	12.9
142		5.8
141		2.1
140		10.5
139		2.9
138		2.1
137	C_2F_2As	42.2
131		3.7
130		2.6
129	C_6F_2	14.5
128		3.6
127	$C_7F_2H_5$	8.3
126		3.0
125	$C_4F_4H_3$	24.0
124		2.1
123	C_7F_2H	3.7

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
122		6.3	91		3.1
121		6.8	90	CH_3As	18.7
			89	CH_2As	52.1
113	AsF_2	23.4	88		9.5
112		2.6			
111		10.1	81		2.6
110	C_6F_2	15.7	80		2.2
109	CH_3AsF	35.5	79		9.3
108		1.0	78		4.6
107		9.1	77		2.6
106		2.1	76		2.6
105	$As(CH_3)_2$	41.7	75	As	9.0
104		2.1	74		2.6
103	$As(CH_2)_2$	19.7	73		2.3
102		4.7	72		13.7
101		6.8	71		13.5
99	C_5F_2H	7.8	69	CF_3	8.4
98	C_5F_2	4.2			
			61		5.6
94	AsF	11.5			
93	C_3F_3	6.8	51		3.1
92		2.1			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γOBS	γ CALC
272	257	242.8	242.83	0.92	0.94
	181	--	--	0.67	0.67
	105	--	--	0.39	0.39
	89	--	--	0.34	0.33
257	255	253.0	253.00	[illegible]	[illegible]
	237	218.7	218.56	0.91	0.92
	181	127.5	127.48	0.70	0.70

MK

m_1	m_2	m*OBS	m*CALC	γOBS	γ CALC
257	163	103.4	103.38	0.61	0.63
	113	--	--	0.45	0.44
	89	--	--	0.35	0.35
255	205	164.8	164.80	--	--
	163	--	--	0.64	0.64
	161	101.7	101.65		0.63
	125	--	--	0.49	0.49
	94	--	--	0.37	0.37
242	223	205.6	205.49	--	--
	125	--	--	0.51	0.52
	113	--	--	0.47	0.47
	94	--	--	0.39	0.39
	75	--	--	0.32	0.31
232	137	--	--	0.58	0.59
	105	--	--	0.45	0.45
	89	--	--	0.38	0.38
217	89	--	--	0.41	0.41
181	161	143.1	143.21	--	--
	94	--	--	0.53	0.52
	79	--	--	0.44	0.44
	71	--	--	0.40	0.39
	32	--	--	0.18	0.18
152	137	123.5	123.48	--	--
137	109	86.7	86.72	--	--
125	75	45.0	45.00	--	--

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
155	C_5F_5	2.2	94		2.8
			93	C_3F_3	6.1
150		0.6			
149		0.6	86	$HPOF_2$	3.9
148	C_6F_4	9.4			
82		0.6	65		7.8
81	CH_3POF	27.8	64		0.6
80		1.7	63	CH_3POH	33.3
79		8.3	62		4.4
78		1.7	61	$(CH_3)_2P$	11.1
77	$(CH_3)_2PO$	45.0	60		1.7
76		4.4	59	$(CH_2)_2P$	16.7
75		8.3	58		1.1
74		2.8	57		2.8
			56		0.6
69	PF_2/CF_3	38.9	55		2.2
68		2.2			
67		13.9			
66		1.1			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	γ CALC
244	229	215.0	214.90	--	--
	209	179.0	179.02	--	--
	179	131.4	131.32	--	--
	163	109.0	108.89	--	--
229	209	190.8	190.75	--	--
	143	89.5	89.30	--	--
228	181	143.6	143.69	--	--
	163	116.6	116.53	--	--
213	211	209.3	209.02	--	--
	163	125.0	124.74	--	--

m_1	m_2	m*OBS	m*CALC	γOBS	MK γ CALC
181	179	177.1	177.02	--	--
179	163	148.2	148.40	--	--
160	111	76.9	77.01	--	--

(22) $C_6F_5P(S)(CH_3)_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
262		6.9	163	$C_7F_4H_3$	15.3
261		14.7	162		2.6
260	$C_6F_5P(S)(CH_3)_2$	100.0	161		8.4
247		4.2	158		1.6
246		6.8	157		2.5
245	$C_6F_5PS(CH_3)$	60.2	156		3.1
			155	C_5F_5	4.9
230		12.6			
229		3.7	150		2.2
228	$C_6F_5P(CH_3)_2$	24.8	149		3.1
227	$C_6F_5P(C_2H_5)$	22.1	148	C_6F_4	4.8
225		4.7	144		7.9
			143	$C_7F_3H_2$	15.2
214		3.7	142		7.9
213	$C_6F_5P(CH_3)$	14.2	141		4.7
212		3.1			
211	C_6F_5PCH	29.8	137	C_5F_4H	4.8
201		1.4	132		2.6
200		4.2	131		2.6
199	C_6F_5S	30.9	130		4.7
			129	C_6F_3	5.2
182		4.5			
181	$C_7F_5H_2$	43.5	125		9.4
180		3.7	124		4.2
179		4.4	123	C_7F_2H	12.6
175		4.7	119		2.1
			118		3.1
168	C_6F_5H	4.8	117	C_5F_3	17.9

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
167	C_6F_5	2.6			
			113		2.6
112		4.2	79	CH_3PHS	30.1
111	C_6F_2H	21.2	78	CH_3PS	11.9
110	C_6F_2	12.0	77		18.2
			76		11.0
99		12.8	75		12.0
98	C_5F_2	9.5	74		4.8
97	CH_3PFS	18.3			
			69	PF_2/CF_3	62.8
95		3.1			
94		4.2	65	CH_3PF	27.8
93	$(CH_3)_2PS/C_3F_3$	56.0	64		4.5
92		4.4	63	PS	72.8
91		2.1	62		2.6
			61	$(CH_3)_2P$	43.2
88	PF_3	2.6	60		3.4
87		3.7	59	$(CH_2)_2P$	27.2
86		4.2	58		6.3
			57		15.5
82		3.4			
81		4.8			
80		5.8			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	γCALC
260	245	230.8	230.87	--	--
	213	174.4	174.50	--	--
245	227	210.4	210.32	--	--
213	211	209.0	209.02	--	--
111	110	108.9	109.01	--	--

(23) $C_6F_5P(Se)(CH_3)_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
311		1.3	244		0.4
310		8.5	243		0.4
309		8.1			
308	$C_6F_5PSe^{80}(CH_3)_2$	54.9	230		0.9
307		3.0	229		11.1
306		36.2	228	$C_6F_5P(CH_3)_2$	100.0
305		9.4	227		59.6
304		14.0	226		0.4
303		0.4	225		1.3
302		0.9			
			214		4.3
295		0.4	213	$C_6F_5P(CH_3)$	46.8
294		0.9	212		66.0
293	$C_6F_5PSe^{80}(CH_3)$	10.2	211	C_6F_5PCH	72.8
292		0.4	210		1.3
291		3.8	209		3.4
290		2.1			
289		2.1	200		3.4
288		0.4	199	C_6F_5PH	46.4
287		0.4	198		2.1
			197		0.9
280		0.4			
279		0.0	194		0.9
278	$C_6F_5PSe^{80}$	2.6	193		1.7
277		0.0	192		0.9
276		0.9			
275		0.4	187		0.4
274		0.4	186		2.6
			185		1.3
249		0.4			
248		0.9	183		0.4

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
247	$C_6F_5Se^{80}$	2.1	182		8.9
246		0.4	181	$C_7F_5H_2$	89.4
245		1.3	180		0.9
179		5.5	129	C_6F_4	4.7
178		0.4	128		1.7
177		0.9	127		3.4
			126		3.4
174		0.9	125	$C_7F_2H_3$	29.8
173		2.1	124		6.0
			123		2.6
168	C_6F_5H	6.4	122		3.4
167		1.3	121		3.0
164		0.4	119		2.1
163	$C_7F_4H_3$	21.3	118		2.1
162		3.4	117	C_5F_3	15.3
161	C_7F_4H	13.2			
160		16.6	113		9.4
159		1.7	112		4.3
158		8.5	111	C_6F_2H	25.5
157		3.0	110	C_6F_2	12.8
156		5.5	109		13.2
155		2.1	108		3.4
154		3.0	107		3.4
			106		1.3
148		3.4	105		4.3
			104		1.7
145		1.7	103		1.3
144		20.9			
143	$C_7F_3H_2$	33.6	100		1.7
142		17.0	99	C_5F_2H	20.0
141		12.8	98	C_5F_2	8.5
140		0.9			
139		5.5	95		3.0
138		1.7	94		4.7

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
137		3.4	93	C_3F_3	17.0
			92		4.7
131		1.7	91		3.8
130		2.6	90		2.1
86		2.6	65		26.0
81		3.8	62		3.0
80	Se^{80}	8.1	61	$(CH_3)_2P$	34.9
79		11.1	60		3.0
78		6.4	59	$(CH_2)_2P$	26.4
77		8.5	58		6.8
			57		13.2
75	C_3F_2H	17.9	56		2.6
74		5.1			
			51		2.6
69	PF_2/CF_3	36.2			

No metastable transitions observed.

(24) $C_{12}F_8P(t\text{-}C_4H_9)$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
385		0.3	323		0.2
384	$C_{12}F_8P(t\text{-}C_4H_9)$	0.6	322		0.2
370		0.4	310		0.3
369	$C_{12}F_8PC_3H_6$	2.0	309	$C_{12}F_7PH$	1.3
			308		0.2
347		0.1			
346	$C_{12}F_6PC_4H_9$	0.3	304		0.1
345		0.1			
344	$C_{12}F_8PC_2H_3$	0.2	297		0.2
			296	$C_{12}F_8$	0.9
329		0.6			
328		4.8	291		0.1
327	$C_{12}F_8P$	19.9			
			289		0.1
279		0.2	205		0.2
278	$C_{12}F_7H$	1.2			
277		0.2	190		0.1
			189	$C_{11}F_3$	0.4
260		0.2			
259		0.9	179		0.2
258	$C_{12}F_6$	4.8			
			177	$C_{10}F_3$	0.1
241		0.2			
240	$C_{12}F_5H$	0.5	105		0.1
239		0.4			
			88	PF_3/C_4H_9P	0.1
228		0.2			
227	$C_{11}F_5$	0.4	69	PF_2/CF_3	0.3
220	$C_{12}F_4$	0.1	65		0.2

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
209		0.2	59		0.2
208	$C_{11}F_4$	0.5	58		8.0
			57	C_4H_9	100.0
			56		1.5
			55		2.0
			54		0.1
			53		0.4

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	γ CALC
328	259	204.0	204.51	--	--
327	258		203.56	--	--
328	240	174.8	175.61	--	--
327	239		174.68	--	--
369	278	209.0	209.44	--	--
258	208	168.0	167.69	--	--

(25) $C_{12}F_8PC_6H_5$

m/e	Ion$^+$	Relative Abundance
406		2.7
405		19.2
404	$C_{12}F_8PC_6H_5$	100.0
403		10.1
402		1.6
388		0.4
387		1.8
386		7.3
385	$C_{12}F_7PC_6H_5$	10.1
384		2.2
378		0.3
377	$C_{12}F_8PC_4H_2$	0.5
374		0.4
373		2.6
372	$C_{18}F_8H_4$	9.8
371		1.8
367		0.4
366		1.6
365	$C_{12}F_6PC_6H_4$	6.4
360		0.4
359		0.6
358		0.3
357		0.3
356		0.4
355		1.9
354	$C_{18}F_7H_5$	9.0
353		0.9
352		0.8
347		0.4
346	$C_{12}F_5PC_6H_3$	0.5
345	$C_{12}F_5PC_6H_3$	0.3
343		0.3
342		0.3
341		0.5
336		0.4
335		1.0
334	$C_{18}F_6H_4$	2.4
333		0.5
332		0.4
329		0.9
328		8.7
327	$C_{12}F_8P$	54.1
323		0.5
317		0.7
316	$C_{18}F_5H_5$	3.4
315		0.8
314		1.0
310		0.5
309		1.1
308	$C_{12}F_7P$	1.2
304		0.3
303	$C_{17}F_5H_4$	0.6
302		0.4

m/e	Ion$^+$	Relative Abundance
292		0.3
291		0.3
290		0.5
289	$C_{12}F_6P$	0.4
286		0.3
285		0.8
284		0.3
283		0.3
279		0.3
278		0.7
277	$C_{12}F_7$	0.6
276		0.3
272		0.3
271		0.3
270		0.2
266		0.5
265	$C_{11}F_7$	0.6
264		0.4
260		0.3
259		2.1
258	$C_{12}F_6$	11.4
256		0.4
255		1.9
247		0.3
246	$C_{11}F_6$	0.4
241		0.3
240		0.8
239	$C_{12}F_5$	1.6
228		0.4
227	$C_{11}F_5$	1.2
221		0.3
220	$C_{12}F_4$	0.5
209		0.5
208	$C_{11}F_4$	1.5
203		0.4
202.5		0.7
202	$C_{12}F_8PC_6H^{++}$	2.4
190		0.4
189	$C_{11}F_3$	1.5
187		0.2
186	$C_{10}F_4$	0.5
179		0.6
108		0.3
107	PF_4	0.6
79		0.4
78		6.4
77	C_6H_5	91.0
76		2.6
75		1.1
69	PF_2/CF_3	1.8
52		3.6
51	C_4H_3	40.9

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γ OBS	MK γ CALC
404	372	342.6	342.54	--	--
	354	310.2	310.18	--	--
403	383	368.0	367.80	--	--
384	365	346.8	346.94	--	--
354	334	315.0	315.13	--	--
327	258	203.7	203.56	--	--

(26) $C_{12}F_8PC_6F_5$

m/e	Ion$^+$	Relative Abundance
496		1.7
495		14.0
494	$C_{12}F_8PC_6F_5$	58.5
476		2.0
474	$C_{12}F_8PC_6F$	8.5
445		1.4
444	$C_{18}F_{12}$	6.2
426		1.1
425	$C_{18}F_{11}$	4.7
407		1.0
406	$C_{18}F_{10}$	2.7
375	$C_{17}F_9$	1.4
365	$C_{12}F_8PF_2$	1.9
356	$C_{18}F_8$	1.0
228		1.0
227	$C_{11}F_5$	5.0
222.5		0.6
222	$C_{18}F_{12}^{++}$	2.4
220	$C_{12}F_4$	1.4
217	C_6F_5PF	1.4
209		1.1
208	$C_{11}F_4$	5.4
337	$C_{18}F_7$	1.4
329		1.5
328		17.5
327	$C_{12}F_8P$	100.0
308	$C_{12}F_7P$	1.6
297		1.1
296	$C_{12}F_8$	6.2
277	$C_{12}F_7$	1.4
260		0.6
259		4.2
258	$C_{12}F_6$	24.5
248		0.5
247.5		1.3
247	$C_{12}F_8PC_6F_5^{++}$	5.6
240		1.0
239	$C_{12}F_5$	4.4
112	C_3F_4	1.2
110	C_6F_2	1.2
105	C_4F_3	1.4
103	C_7F	1.3
93	C_3F_3	1.2
91	C_6F	1.4

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
			81	C_2F_3	1.4
189	$C_{11}F_3$	1.1			
188	C_3F_7P	6.5	69	PF_2/CF_3	9.3
179	C_7F_5	1.5			
129	C_6F_3	2.2			
117	C_5F_3	1.9			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	γ CALC
494	475	457.0	456.73	--	--
	444	399.2	399.06	---	--
406	387	368.6	368.89	---	--
327	259	205.0	205.14	---	--

(27) $C_{12}F_8Co(\pi\text{-}C_5H_5)CO$

m/e	Ion$^+$	Relative Abundance
450		0.5
449		4.0
448	$C_{12}F_8Co(C_5H_5)CO$	16.2
429		0.3
428	$C_{12}F_7Co(C_5H_4)CO$	0.5
422		0.5
421		2.4
420	$C_{12}F_8Co(C_5H_5)$	9.6
402		0.5
401		1.2
400	$C_{12}F_7Co(C_5H_4)$	3.9
382		0.5
381		1.0
380	$C_{12}F_6Co(C_5H_3)$	3.4
363		0.2
362	$C_{12}F_5Co(C_5H_4)$	1.5
361		0.7
360	$C_{12}F_5Co(C_5H_2)$	2.0
359		0.6
344		0.6
343		2.0
342	$C_{12}F_4Co(C_5H_3)$	7.0
341		3.3
324		3.6
323	$C_{17}F_6H_5$	10.1
322		1.7
321		1.6
311		0.5
310		1.3
309		0.6
305		0.9
304		2.3
303	$C_{17}F_5H_4$	4.9
299		1.6
298	$C_{12}F_8H_2$	10.3
297		1.5
296	$C_{12}F_8$	2.1
293		0.8
292		2.3
291		1.3
261		0.5
260		1.0
259		1.3
258	$C_{12}F_6$	3.1
248		0.5
247	$C_{11}F_6H$	1.2
246		0.7
241		0.5
240		0.8
239	$C_{12}F_5$	1.0
219		1.9
218		0.8
217		1.9

m/e	Ion$^+$	Relative Abundance
210		1.9
209		1.0
208		1.3
190		1.0
189		4.0
150		0.6
149.5		0.5
149	$C_{12}F_8H_2^{++}$	3.1
131		2.0
125		6.0
124	$Co(C_5H_5)$	100.0
123		1.7
119		1.6
103		4.1
100		0.6
99		1.1
98	$Co(C_3H_3)$	7.0
97		1.6
93	C_3F_3	1.4
92		0.5
91		1.1
86	C_4F_2	1.6
85		1.1
84		2.8
71		0.7
70		0.5
69	CF_3	7.4
66		4.4
65	C_5H_5	5.3
64		0.8
63		2.5
62		0.9
61		0.7
59	Co	14.0
58		6.0

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	MK γ CALC
448	428	409.0	408.89	--	--
420	400	381.0	380.95	--	--
380	360	341.1	341.05	--	--

(28) $C_{12}F_8Rh(\pi\text{-}C_5H_5)CO$

m/e	Ion$^+$	Relative Abundance
494		0.4
493		1.9
492	$C_{12}F_8Rh(C_5H_5)CO$	8.2
466		0.9
465		6.8
464	$C_{12}F_8Rh(C_5H_5)$	28.5
463		0.7
462		1.3
447		0.8
446		3.4
445		0.6
444	$C_{12}F_7Rh(C_5H_4)$	1.2
443		0.3
442		0.6
424		0.7
360	$C_{17}F_8H_4$	0.6
342		0.7
341	$C_{17}F_7H_4$	1.0
328		0.7
324		0.5
323	$C_{17}F_6H_5$	0.8
322		0.5
321		0.6
315		0.4
304		0.3
303	$C_{17}F_5H_4$	0.6
299		0.6
298	$C_{12}F_8H_2$	3.6
297		0.5
296	$C_{12}F_8$	1.0
292		0.6
291		0.5
280	$C_{12}F_7H_3$	0.9
279		0.5
278		0.7
277	$C_{12}F_7$	0.4
260		0.6
234		0.6
233		3.1
232.5		0.4
232	$C_{12}F_8RhC_5H_5^{++}$	1.2
229		0.8
169		9.2
168	$Rh(C_5H_5)$	100.0
151		0.9
149		1.4
142	$Rh(C_3H_3)$	9.4

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
310		0.6			
127		0.8	86		0.5
126		0.6	85		3.1
125		1.8	84		1.1
124		0.7	83	C_5H_4F	3.7
123		1.5	82		1.2
			81		2.2
115		0.9			
			71	C_4FH_4	4.2
113		1.3	70		1.5
112		1.1	69	CF_3	3.2
111		2.9			
110		0.9	67		1.1
109		2.1	66		1.4
			65	C_5H_5	1.5
103	Rh	10.7			
			58		1.6
99		1.4	57	C_3FH_2	5.9
98		0.9	56		1.2
97		3.9	55	C_3F	2.2
96		1.3			
95		2.5			

Metastable Transitions

m_1	m_2	m*OBS	m*CAlC	MK γ OBS	γCALC
492	464	437.8	437.59	--	--
464	444	424.7	424.86	--	--
464	168	60.8	60.83	--	--
444	424	404.8	404.90	--	--
341	321	301.9	302.17	--	--
323	233	167.8	168.08	--	--
168	142	120.0	120.02	--	--
168	103	63.2	63.15	--	--

(29) $C_{12}F_8Ir(\pi\text{-}C_5H_5)CO$

m/e	Ion$^+$	Relative Abundance
584		1.0
583		5.5
582	$C_{12}F_8Ir^{193}(C_5H_5)CO$	26.3
581		4.3
580		15.6
556		3.5
555		19.9
554	$C_{12}F_8Ir^{193}(C_5H_5)$	100.0
553		14.2
552		61.9
551		2.5
536		1.5
535		0.9
534	$C_{12}F_7Ir^{193}(C_5H_4)$	1.7
533		1.7
532		3.6
531		1.0
530		2.0
515		1.9
514	$C_{12}F_6Ir^{193}(C_5H_3)$	9.4
513		3.6
512		7.1
511		1.2
510		2.3
509		2.7
508		1.7
507		3.0
506		1.1
505		1.7
496		0.6
495		1.6
494	$C_{12}F_5Ir^{193}(C_5H_2)$	4.3
493		1.5
492		3.0
490		1.4
489	$C_{12}F_8Ir^{193}$	5.9
488		4.6
487		4.9
486		2.7
482		2.0
480		1.0
440		1.8
439	$C_{1f}F_6Ir^{193}$	6.9
438		1.6
437		4.9
421		1.3
420	$C_{11}F_5Ir^{193}$	2.3
419		1.3
418		1.6
390		0.7
389	$C_{10}F_4Ir^{193}$	3.5
388		0.7
387		2.6
342		0.9
341	$C_{17}F_7H_4$	2.0

m/e	Ion$^+$	Relative Abundance
329		0.6
328	$C_{16}F_7H_3$	4.0
324		1.0
323	$C_{17}F_6H_5$	3.7
316		0.6
315		1.7
311		1.1
310	$C_{16}F_6H_4$	3.0
309		1.8
299		1.8
298	$C_{12}F_8H_2$	11.2
292		1.7
291	$C_{16}F_5H_4$	3.5
290		2.4
278		4.3
277.5		4.3
277	$C_{12}F_8Ir^{193}(C_5H_5)^{++}$	22.0
276.5		4.6
276		9.4
260		1.5
259		1.4
258	$C_{12}F_6$	7.7
257		2.7
256		5.8
255		2.2
254		3.3
230		6.8
229		3.5
229		4.8
227		2.3
182		0.5
181	$C_7F_5H_2$	3.7
169		2.9
168	C_6F_5H	4.7
151		1.1
150		1.2
149	C_6F_4H	2.4
133		0.6
132		0.7
131	$C_6F_3H_2$	4.9
120		0.6
119	$C_5F_3H_2$	5.6
105		1.3
104		1.6
103		6.6
93	C_3F_3	2.7
79		1.9
78	$C_3F_2H_4$	24.1
77		5.4
76		3.8
75		1.9

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
232		3.5	71		1.6
231		3.2	70		1.1
69	CF_3	39.2	59	C_3FH_4	13.5
68		1.0	58		8.8
67		1.8	57		6.6
66		3.6	56		3.6
65	C_5H_5	7.3			
64		1.4			
63		3.1			

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	γOBS	MK γ CALC
582	554	527.0	527.35	--	--
580	552		525.35	--	--
554	514	475.5	476.89	--	--
552	512		474.90	--	--
489	439	393.5	394.11	--	--
487	437		392.13	--	--
439	389	344.5	344.69	--	--
437	387		342.72	--	--

(30) $C_{12}F_8Ti(\pi\text{-}C_5H_5)_2$

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
477		0.5	458		0.4
476		2.6	457		1.6
475		5.3	456		7.0
474	$C_{12}F_8Ti^{48}(C_5H_5)_2$	16.6	455	$C_{12}F_7Ti^{48}(C_5H_5)_2$	18.5
473		2.9	454	$C_{12}F_7Ti(C_{10}H_9)$	49.9
472		2.3	453		8.2
			452		6.5
411		0.3	322		2.3
410		0.4	321		2.1
409	$C_{12}F_8Ti(C_5H_5)$	1.3			
408		0.3	319		0.6
407		0.1	318		0.8
			317		1.6
369		0.8	316		0.7
368		1.7	315		0.6
367	$C_{22}F_5H_8$	2.4			
366		3.3	312		0.6
			311		1.4
355		0.2	310		1.4
354		0.6	309		1.2
353	$C_{21}F_5H_6$	1.1			
			306		0.6
350		1.5	305		1.4
349		3.7	304		6.4
348		9.6	303		18.2
347		1.4	302		2.1
346		1.6	301		1.5
344		0.5	299		1.7
343		1.3	298	$C_{12}F_8H_2$	2.7
342	$C_{17}F_7H_5$	2.8	297	$C_{12}F_8H$	2.3
341		1.7			
340		0.8	293		1.2
			292		2.3

m/e	Ion$^+$	Relative Abundance	m/e	Ion$^+$	Relative Abundance
331		1.2			
330		3.0	287		0.7
329		2.1	286		2.8
328		2.6	285		11.2
327		1.4	284		3.7
			283		5.0
325		0.6			
324		2.3	278	$C_{12}F_7H$	2.3
323	$C_{17}F_6H_5$	5.4	277	$C_{12}F_7$	2.4
273		1.4	209		1.1
272		2.3	208		1.2
261		0.6	195		0.9
260		1.0	194		1.7
259		2.8			
258		1.9	190		1.2
257		0.9	189		5.9
256		0.6			
255		0.9	182		0.5
254		3.1	181		1.6
253		2.3	180		0.8
252		1.8	179		0.6
			178		6.6
247		0.9	177		0.9
246		1.0	176		0.9
241		1.1	171		1.9
240		1.0	170		2.4
239		1.9	169		1.5
237		1.3	166		0.5
236		1.0	165		1.9
235		1.9	164		1.0
234		1.6			
233		1.3	153		2.3

m/e	Ion$^+$	Relative Abundance
231		0.7
230		0.4
229		0.9
228		1.2
227		1.6
214		0.7
213		0.6
212		1.6
125		2.3
115		0.9
114		1.7
113	$Ti(C_5H_5)$	7.7
112		2.3
111		1.7
107		1.3
106	C_4F_3H	7.3
105	C_4F_3	2.6
104		1.7
103		5.9
94		0.8
93	C_3F_3	4.2
92		1.8
91		2.2
88		1.4
87		3.3
86	TiF_2	13.4
85		2.3
84		2.1
152		3.7
151	$(C_5H_5)TiF_2$	16.3
150		2.8
149		2.5
147		0.9
146		1.6
134		9.8
133		16.1
132	$(C_5H_5)TiF$	100.0
79		1.6
78		12.3
77		4.0
76		3.5
75		2.1
74		1.6
69	CF_3	6.6
67		7.1
66		5.0
65	C_5H_5	8.0
64		1.5
63	C_5H_3	3.3
62		2.0
61		1.6
59		1.3
58		17.3

Metastable Transitions

m_1	m_2	m*OBS	m*CALC	MK γOBS	MK γ CALC
474	454	435.0	434.84	--	--
474	409	353.0	352.91	--	--
474	367	284.0	284.15	--	--

APPENDIX B

Metastable Ions

In sector-type instruments such as the MS-30 (see schematic Fig. 2), decompositions of the form $m_1^+ \rightarrow m_2^+ + m_3$, occur between the ion source and the magnetic analyzer. Here m_1^+ is an arbitrary ion of mass m_1 which decomposes to an ion of mass m_2 and a neutral fragment $m_3 = m_1 - m_2$. If this dissociation occurs with a very small release of internal energy and m_2 and m_3 have the same or nearly the same resultant velocities then this transition gives rise to a peak at a mass $m^* = m_2^2/m_1$.

Observation of these metastable ions is most favoured when the decomposition occurs in the β-region. At this point the ions have already been analyzed electrostatically and the ion m_1 will have a velocity given by

$$1/2 m_1 v2 = eV \quad (1)$$

where v is the velocity, e is the charge on the ion and V is the accelerating potential. Decomposition by the pre-described pathway gives an ion m_2 with a velocity of

$$1/2 m_2 V^2 = \frac{m_2}{m_1} eV \quad (2)$$

Mass analysis by the magnetic sector follows the equation $BeV = \frac{mV^2}{R}$ (3) which gives with (2) on elimination of V

$$\frac{m_2^2}{m_1} \cdot \frac{1}{e} = \frac{R^2 B^2}{2V}$$

One can easily see that this is the exact equation for

analysis of a corresponding mass m*

$$\text{i.e.} \quad m^*/e = \frac{R^2B^2}{2V} \quad \text{where } m^* = \frac{m_2^2}{m_1}$$

If the dissociation occurs somewhere during electrostatic analysis, the ion m_2 will arise from this sector with a velocity given by

$$1/2m_2v^2 = \frac{m_2}{m_1} eVo + e(V_1-Vo)$$

where Vo is the potential difference acting on m_1 before decomposition and V_1 is the potential exerted on m_2. This gives a final value for m* as indicated

$$m^* = \frac{m_2^2}{m_1} \left(1 + \frac{(m_1-m_2)(V_1-Vo)}{m_2V_1}\right)$$

Since the conditions existing in the mass spectrometer are far from ideal (decompositions often proceeding with released internal energy) the bulk of the resulting ions do not reach the mass analyzer and this explains the diffuse, low intensity peaks normally obtained for "metastable" ions. This latter feature provides the motive for establishment of metastable defocusing techniques in order to enhance sensitivity in the detection of these useful entities.

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* Note: This set of six volumes is an excellent comprehensive review of organophosphorous compounds including references to preparation, reactions and physical and spectroscopic properties.